REMOVAL OF AMMONIA FROM WASTEWATER BY ION EXCHANGE IN THE PRESENCE OF ORGANIC COMPOUNDS

A THESIS PRESENTED FOR THE DEGREE OF MASTER OF ENGINEERING IN CHEMICAL & PROCESS ENGINEERING

TONY C. JORGENSEN

2000 - 2002

Department of Chemical & Process Engineering
University of Canterbury
Christchurch, New Zealand

We don’t have much money to do this so we are going to have to think.

Lord Ernest Rutherford

ABSTRACT

The aim of the work described in this thesis was to study the removal of ammonium ions from water by ion exchange. The classical technique is to use biological nitrification and denitrification to convert ammonia into nitrogen gas. Removal by ion exchange offers a number of advantages, such as the ability to handle shock loadings and to polish water to a very high specification.

The ion exchanger used in this project was clinoptilolite, a naturally occurring zeolite. Previous research has included characterisation of clinoptilolite, the effect of other common cations on uptake, biological regeneration, and a few other studies. A comparison with other exchangers was also conducted.

Much of the available literature is concerned with clinoptilolite and occasionally with mordenite, however modern ion exchangers are polymer based. Two polymeric ion exchangers (Dowex 50w-x8, and Purolite MN500) were evaluated in this project.

The main scope of this thesis was to look at the effect that organic pollutants has on ammonium ion removal during ion exchange.

The results of batch equilibrations of NH_4^+ and the three exchanger resins can be seen in chapter 4.0. They show that the presence of an organic compound enhanced the uptake of NH_4^+ in most cases onto clinoptilolite and Purolite MN500. There was no apparent uptake onto Dowex 50w-x8. Further experiments with a sample of real industrial wastewater (woolscour wastewater) showed varied results, showing that each site should carry out its own pilot scale testing during plant design.

Other experimental work showed that the exchanger resins adsorb little or none of the organic compounds in solution. These results can be seen in chapter 5.0.

Studies in a packed column showed that the presence of organic compounds had little or no effect on NH_4^+ removal. There was however an increase in capacity after each regeneration of the bed and continued removal after breakthrough. The same results were achieved in the control experiment with no organic compounds present, hence these results are not related to the presence of an organic compound. The presence of NH_4^+ and various compounds did however provide micro-organisms with substrates from which to grow causing hydraulic difficulties in the column. See chapter 6.0 for these results.

The final section of experimental work studied whether the presence of organic compounds changed the rate of uptake of NH_4^+. The results in chapter 7.0 show that there was no effect on the rate of NH_4^+ uptake.

ACKNOWLEDGMENTS

- Firstly I would like to thank my supervisor Professor L. R. Weatherley, whose guidance helped me set very high standards. His expertise was instrumental towards the project and included a number of original and novel ideas.

- My thanks must also be extended to a number of others. The first would be to Trevor Berry for his excellent and immediate help on many occasions and his expertise of the entire department. No matter what problem or question was thrown at him he always had the answer.

- The technicians Frank Weerts, Ron Boyce, and Paul Tolson for their help with the design and construction of the ion exchange columns. Tony Allen for correcting all computer problems.

- Purolite for supplying us with a sample of the hyper-cross-linked macronet resin (MN500).

- Kiwi Dairies for the sample of whey protein.

- Dryden aquaculture for the clinoptilolite.

- Last but certainly not least to Cherry for keeping me sane through the long nights spent in the laboratory.

CONTENTS

Page number

1.0 INTRODUCTION

1.1 WASTEWATER AND THE ENVIRONMENT

Approximately 100 years ago in Chicago the town water supply intake pipes were moved 4 miles from the shore of Lake Michigan [12]. As a result of this the mortality rate from typhoid fever dropped by 80%. This came about because the sewage was released further away from the point of abstraction for the water supply.

Pathogens are commonly waterborne and can be passed on to humans orally, thus causing disease. Organic and nitrogenous pollutants cause eutrophication and the growth of pathogens when released into waterways, as a result aquatic life can be harmed. Waterways are also used as town water supplies, passing on cholera, typhoid fevers, and many other diseases [12].

In the above example the outlet pipe was moved further from the water resources of the population. Water and atmospheric wastes need treatment before disposal. Legal regulations are becoming more stringent, and enforced, to make sure this happens.

1.1.1 Ammonia in wastewater

Municipal and industrial wastewaters contain a complex mixture of pollutants. One of the common, toxic pollutants is ammoniacal nitrogen (NH_3 and NH_4^+). Ammonia is either initially in wastewater or is present as a product of biological oxidation of organic nitrogen. Nitrogen is found in proteins, amines, urea and other organic compounds. Therefore quantities of ammonia present can be substantial after biological oxidation of organic pollutants.

As awareness of wastes in water has grown over the past century, so to have the necessary controls on release. The Council of European committees has set a guide level of 0.05mg/l and a maximum level of 0.5mg/l of ammonia for ammonia discharge. The American Committee on Water quality recommended a limit of 0.02mg/l of ammonia [31]. New Zealand discharge standards vary from 0.22mg/L to 0.77mg/L for release into receiving waters [50].

Ammonia is also known to be very toxic for fish; concentrations as low as 0.2mg/l to 0.5mg/l can be fatal [16,18]. In New Zealand, outlets from dairy farm oxidation ponds were found to have ammonia concentrations of ~75mg/l, and from piggery farms levels can be in excess of 200mg/l [50]. Concentrations such as these are unacceptable for discharge into receiving waterways.

Ammoniacal nitrogen is present in two forms when in water; ammonia (NH_3) or ammonium (NH_4^+), according to Equation 1.1.

$$\mathbf{NH_4^+ + OH^- \Leftrightarrow NH_3 + H_2O} \quad . \quad . \quad . \quad (1.1a)$$

$$\mathbf{NH_3 + H_3O^+ \Leftrightarrow NH_4^+ + H_2O} \quad . \quad . \quad . \quad (1.1b)$$

The balance of the equilibrium of the ammoniacal nitrogen is dependent on temperature, but more so on pH. The percentage of ionised ammonia, as a function of pH, can be seen in Figure 1.1.

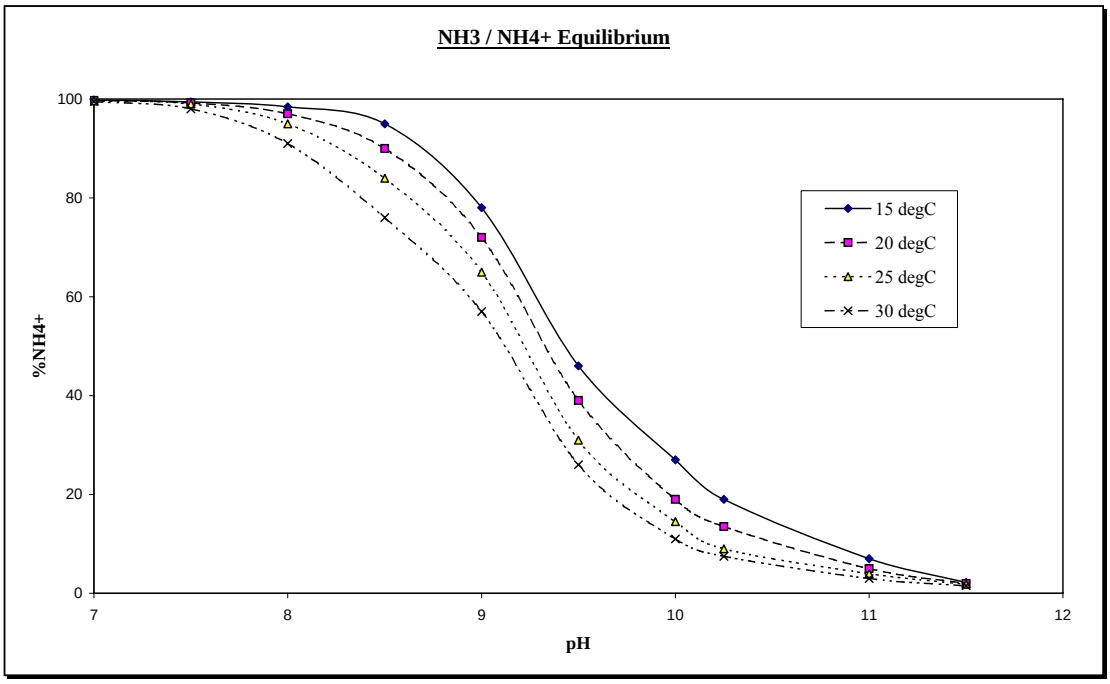


Figure 1.1: pH/temperature equilibrium of NH_3/NH_4^+ [16,18,21].

Ammonia (unionised form) is generally more toxic to plants and animal life than the ionised form. Therefore at low pH the concentration of ammonia can almost be ignored, however if the pH is too low**,** plant and animal life will suffer from acidic toxicity.

Ammoniacal nitrogen also contributes to BOD in water. Nitrifying bacteria require a large amount of dissolved oxygen to convert NH_3 into NO_3^- (4.3mg of O_2 for every 1.0mg of NH_3). Dissolved oxygen levels are commonly 8-10mg/l and fish require at least 5mg/l. Therefore not only is NH_3 toxic but its presence also significantly reduces the level of dissolved oxygen in slow flow rivers and lakes. In turbulent waters this is less of a problem [2,12].

If NH_4^+ is released into waterways it will be degraded into nitrites and nitrates (NO_2^-, NO_3^-). Nitrates stimulate algal growth and eutrophication in waterways. Nitrates in

drinking water cause methemoglobinemia in infants (blue babies). The presence of nitrates can also lead to the formation of carcinogenic nitrosamines [2, 12, 21].

Figure 1.2 shows the nitrogen cycle in the environment. The organic-nitrogen degradation, nitrification and denitrification steps can be seen in the lower left hand corner.

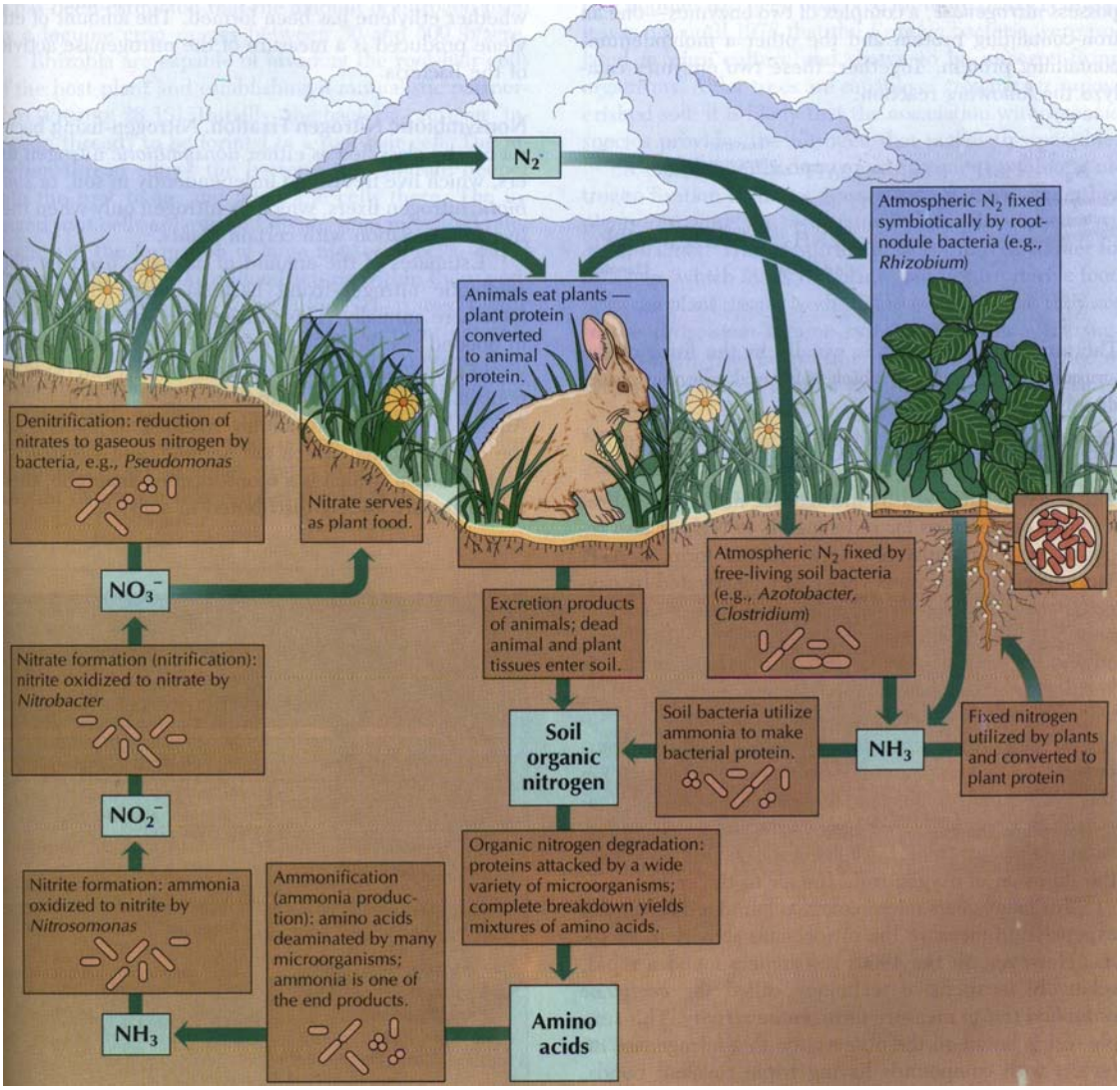


Figure 1.2: Nitrogen cycle [7].

1.2 AMMONIA REMOVAL METHODS

The most common method for the removal of ammonia from wastewater is biological nitrification followed by denitrification, which converts NH_3 into NO_3^-, then N_2. Ion exchange is the method examined in this study.

1.2.1 Ion exchange

References for ion exchange can be found as far back as biblical times. As the understanding of ion exchange has grown so to has its use as an industrial unit operation. Common industrial applications include water softening, boiler feed water treatment, and heavy metal removal [1,9,11].

The first known ion exchangers used soils and sands [1]. As the understanding and popularity of ion exchangers grew over the last few decades many synthetic exchangers have been developed. The first ion exchangers used natural zeolites, now there are synthetic zeolites and polymeric ion exchangers.

Ion exchangers are insoluble resins that contain soluble and mobile exchangeable ions. When the resin comes in contact with water the ion dissociates and becomes mobile, though exchange may occur providing there are ions in the aqueous phase which can replace those on the exchanger and thus maintain overall charge neutrality.

Hence, if other ions are present in the aqueous phase they can exchange with the mobile ions in the resin. The overall charge must be maintained otherwise the resin will attract or repel ions to maintain the charge balance. Co-ions (the anion during cationic exchange) do not normally enter the resin as the charges of the co-ion are the same as the charges on the resin, hence they repel each other (Donnan exclusion).

Concentrations therefore build up at the bead surface but decrease as exchange proceeds. It is possible though for neutral species to enter the resin especially if the solution is concentrated (Donnan invasion).

1.2.1.1 Ion exchange equilibrium

Figure 1.3 shows how equilibrium is established when an ion exchanger containing "A" ions comes in contact with "B" ions in an aqueous solution.

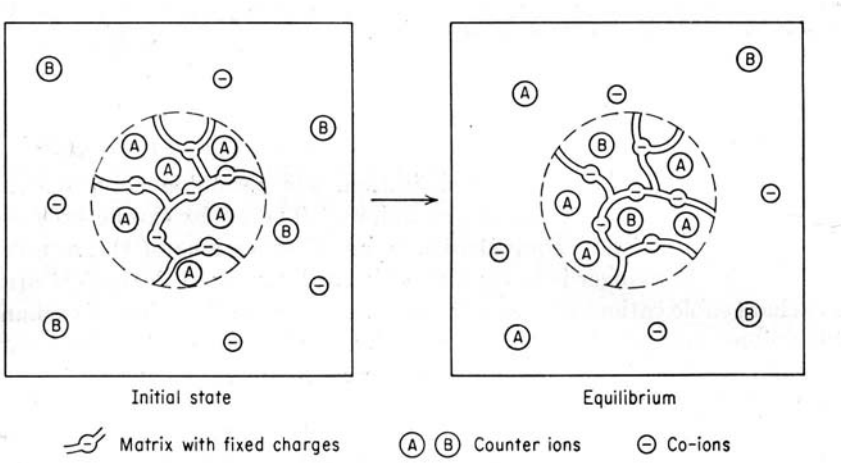


Figure 1.3: Ion exchange equilibrium [1].

When the resin comes in contact with ions in the aqueous phase equilibrium may be established. The equilibrium concentrations are difficult to predict because inside the resin there are high concentrations of charged groups [10].

$$A^{+}_{r} + B^{+}_{aq} \leftrightarrow A^{+}_{aq} + B^{+}_{r} \quad . \quad . \quad . \quad . \quad . \quad (1.2)$$

Ion transport inside the exchanger is diffusion controlled and occurs through pores or voids and within the polymeric matrix of the resin. Resins can swell or shrink to accommodate differences in hydrated ion size and osmotic pressure.

Ion exchange equilibria may be modelled with the Langmuir and Freundlich isotherm models. These two models were originally developed for adsorption, although due to the similarities between adsorption and ion exchange they are also commonly used for ion exchange. More detail on these two models can be found in section 1.3.

1.2.1.2 Ion exchange in packed columns

Ion exchange equilibria is an important consideration in understanding ion exchange column behaviour.

As an influent begins passing into an ion exchange bed the first resin beads will exchange ions until exhaustion. The exchanging zone then moves through the column until it reaches the outlet, i.e. breakthrough.

Figure 1.4 shows a common breakthrough curve at three different flowrates. A high flowrate is associated with early breakthrough and a wide (non-sharp) breakthrough curve. Low flowrates may be associated with later breakthrough and a narrow (sharper) breakthrough curve. At low flowrates a greater volume of water may be treated until breakthrough occurs, however it is slower thus requiring larger columns.

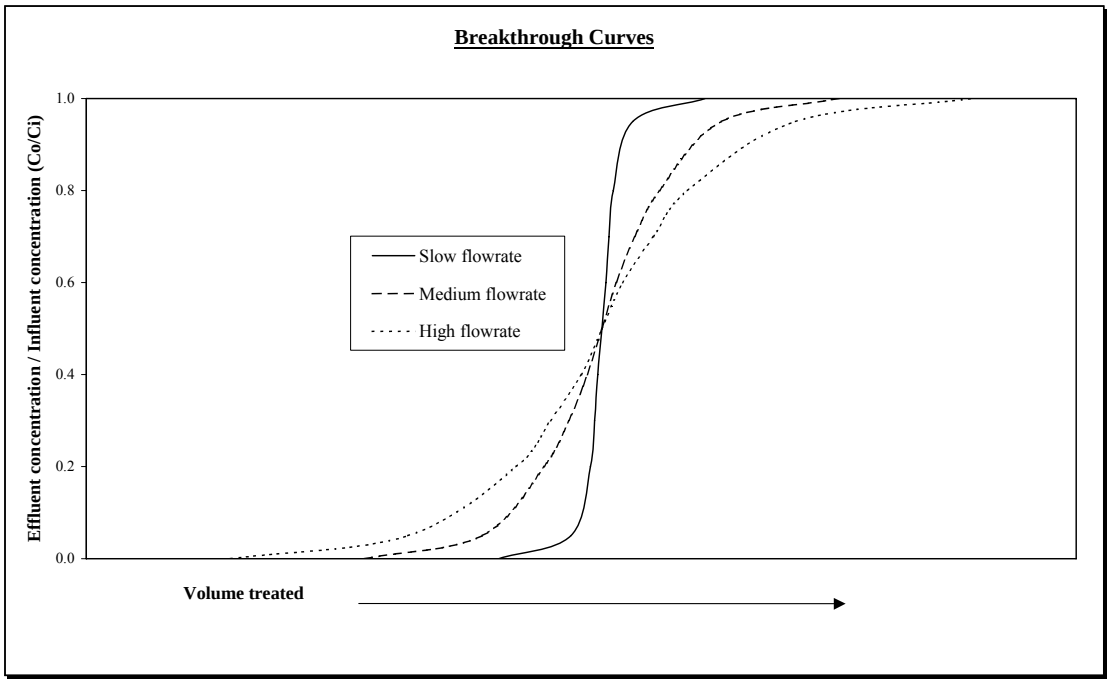


Figure 1.4: Breakthrough curve showing the outlet concentration.

Figure 1.5 shows schematically a mass transfer zone (MTZ) moving through a fixed bed of ion exchange. Initially the bed is in the 'A' form; influent 'B' ions then displace the 'A' ions. Depending on the selectivity the MTZ can sharpen or widen as it moves through the bed. If the resin prefers 'B' ions the MTZ will sharpen, and widen if the resin prefers 'A' ions.

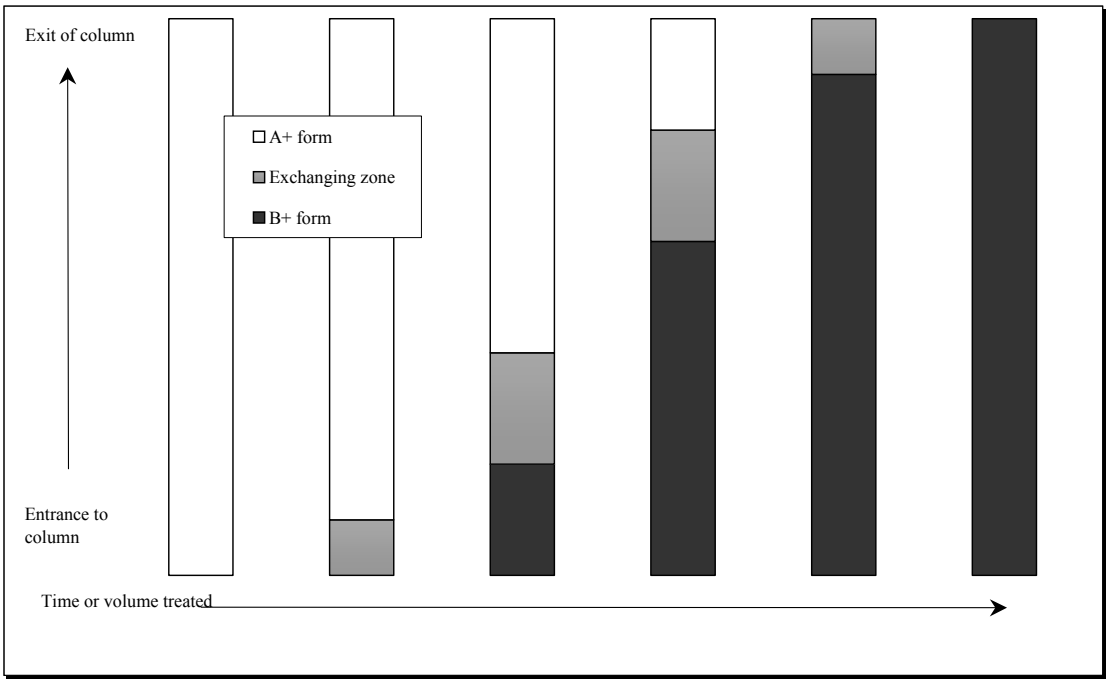


Figure 1.5: Mass transfer zone (exchanging zone) moving through a fixed bed.

Column operation is discontinued usually when breakthrough begins to occur. It is therefore preferable to have a sharp MTZ so that most of the bed is utilised. Previous studies [18,50] have found that smaller particle diameter and slower flowrate allow more water to be treated before breakthrough of the bed occurs, due to a narrower MTZ being achieved under these conditions. If however particles are too small then the pressure drop through the column may be unacceptably high, channelling can also occur.

A treatment plant is likely to have more than one column so they can be arranged in series, parallel, or a mixture. This means that treatment of water can still occur while some columns are out of service for regeneration etc. It also gives greater flexibility to the process during periods of high or low flowrate.

Bed depth service time model

The bed depth service time model can be used to predict breakthrough of a packed bed during ion exchange or adsorption [11,18], see Equation 1.3. It assumes that the adsorption rate is proportional to the residual adsorbent capacity and the adsorbate concentration.

$$t = \left(\frac{N_o}{c_o u}\right) * \left[L - \left(\frac{u}{kN_o}\right) * \ln\left(\left(\frac{c_o}{c_b}\right) - 1\right)\right] \quad . \quad . \quad . \quad . \quad (1.3)$$

t = Service time
u = Linear velocity
L = Bed length
k = Rate constant
N_o = Adsorptive capacity
c_o = Influent concentration
c_b = Breakthrough concentration
(Any consistent units can be used)

1.2.1.3 Regeneration

Ideally ion exchange is a reversible process, and therefore once a bed becomes exhausted or breakthrough occurs, the bed is usually regenerated and the resin is returned to its original ionic form so it can be reused.

Chemical regeneration

Therefore, once the effluent reaches the maximum permissible concentration level the ion exchanger is taken out of service for regeneration. A solution containing a high concentration of the original ions is then passed through the column. After regeneration, the resin is subject to washing with pure water to remove loosely bound ions and traces of the regenerant solution.

Regeneration is not an easy process as ions with a lower affinity are displacing those with a higher affinity from the resin. Therefore regeneration may not usually be taken to completion, and the degree of regeneration is determined by economics. Regeneration is where a significant part of the operating cost of ion exchange lies.

In the case of this project the exchanger resin is initially in the sodium form (Na^+), and the influent contains NH_4^+ ions. During a cycle the NH_4^+ ions will displace the sodium ions and after time breakthrough will begin to occur. At this point flow to the column is stopped and regeneration begins. Sodium chloride solution was the regenerant used.

In most other regeneration situations a high concentration of regenerating ions are required to displace the ions attached during the service cycle due to the higher affinity for these ions over the regenerant ions. However in this case NH_4^+ ions are easily removed because at high pH the displaced NH_4^+ ions are converted to NH_3 molecules. The NH_3 molecules can not exchange back onto the resin. The disappearance of NH_4^+ ions from solution favours the equilibrium to drive more NH_4^+ ions off the resin. Therefore alkaline regeneration requires a smaller volume of regenerant than NaCl only regeneration.

The regenerant solution is usually a mixture of NaCl (provides bulk of Na^+ ions) and NaOH (provides high pH). The caustic conditions also sterilise the resin during regeneration. Under alkaline conditions not only is the equilibrium pushed to

completion but the kinetics are much faster due to the disappearance of NH_4^+ ions. Due to the ease of regeneration NH_4^+ treatment by ion exchange is a very suitable method relative to other ion exchange applications.

Of the initial regenerant solution, some of the Na^+ ions are placed onto the resin and equi-molar amounts of OH^- ions are utilised to convert NH_4^+ ions into NH_3. Therefore a small amount of NaOH is required to return the regenerant solution to its initial form.

Reconditioning of the regenerant solution

Air stripping can be used in the reconditioning of the regenerant solution as the pH is already high and will not need neutralisation back to 7.0. Ion exchange effectively concentrates the ammonia from a very large volume during the service cycle, into a very small volume during regeneration. The ammonia is stripped by air from the regenerant solution (most likely in a packed tower) until a sufficiently low concentration is achieved. The gaseous NH_3 can then be passed through acidic water or a biofilter so that ammonia is not released to the environment [18,21].

Reconditioning of the regenerant solution significantly reduces the operating cost, allowing it to be reused. NH_4^+ can also be precipitated by the RIM-NUT process, which allows the NH_4^+ rich precipitate to be used for fertiliser [21].

Other common cations will also be displaced during regeneration such as Ca^{2+}, Mg^{2+}, and K^+. Ca^{2+}, Mg^{2+}, will however precipitate under the alkaline conditions of regeneration and could slowly foul the resin. Precipitation will however remove these ions from the regenerant solution. If fouling does cause a problem then an extra step in regeneration may be required (such as acid treatment) to remove Ca^{2+}, Mg^{2+} deposits from the resin.

A literature search in a previous study [16] found that there was no practical method by which K^+ ions could be removed from the regenerant solution.

Biological regeneration

Biological regeneration is another method to remove NH_4^+ from spent resins [18, 21]. $NaHCO_3$ is passed through the column where the Na^+ ions displace NH_4^+ ions. Nitrifying biomass then consumes the desorbed NH_4^+. The bicarbonate supplies carbon to the biomass and also stops the pH from dropping too low. Approximately two moles of $NaHCO_3$ are required for each NH_4^+ ion consumed to maintain a suitable pH.

Usually extra Na^+ ions (e.g. NaCl) are required to displace more NH_4^+ ions for nitrifiers. The extra Na^+ ions are also required to displace other cations (Ca^{2+}, K^+, etc) that were present in the influent. This is because biological regeneration only removes NH_4^+ ions.

Thermal regeneration

Another regeneration method is thermal regeneration [14]. Spent resin in the NH_4^+ form is heated to between 300°C-600°C. At these temperatures NH_3 is driven off and the resin is left in the H^+ form. Problems with this method include:

- Incomplete regeneration
- Damage to the structure of the zeolite at high temperatures
- Other cations are not displaced (e.g. Ca^{2+}, Mg^{2+}, and K^+)

- The effluent during service will have a low pH.

Because of thermal degradation, this method is only useful for zeolites and not for polymeric exchangers.

1.2.1.4 Selectivity in ion exchange

In binary systems the selectivity is a measure of the preference that the ion exchanger has for one ion over the other (see Equation 1.4).

The selectivity of A relative to B is:

$$\alpha_B^A = \frac{\vec{A}B}{\vec{B}A} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1.4)$$

Where $\vec{A}$ and $\vec{B}$ refer to the mole fraction in the solid phase, and A and B are the mole fractions in the aqueous phase. Values of α_{AB} greater than 1.0 indicate preferential equilibrium uptake of A relative to B. Values of α_{AB} less than 1.0 indicate preferential equilibrium uptake of B relative to A.

Selectivity is also described by an isotherm of mole fractions on one of the components. The mole fraction on the solid phase (y-axis) is plotted against the liquid phase mole fraction (x-axis).

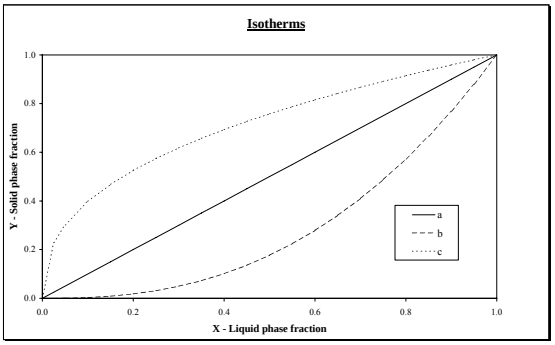


Figure 1.6(a): Binary isotherm, mole fractions.

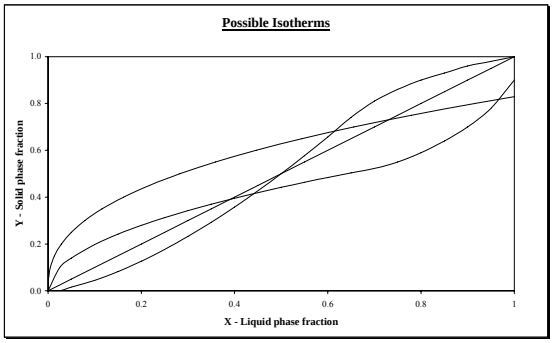


Figure 1.6(b): Other possible isotherms.

In Figure 1.6(a) isotherm 'c' indicates the preferred ion. Isotherm 'a' is where each ion has the same selectivity. Isotherm 'b' indicates the ion which is not preferred.

Not all isotherms are as simple as that shown in Figure 1.6(a). A number of other complex possibilities can exist, some of which are shown in Figure 1.6(b) where selectivity cross-over is shown. This behaviour is quite common in zeolites, but less common for polymeric resins. Selectivity cross-over can be limited to the structural characteristics of zeolites [16].

Isotherms can exhibit hysteresis. If the resin is in the 'A' form and it is contacted with a solution containing 'B' ions an isotherm can be plotted. A different isotherm will results if the resin starts in the 'B' form and is contacted with a solution of 'A' ions.

There is also the case where the ion exchange is not completely reversible. If a resin is in the 'A' form and is contacted with 'B' ions the maximum uptake can differ if the resin is in the 'B' form and is contacted with 'A' ions (see the isotherms in Figure 1.6(b) that do not cross (1,1)).

1.2.1.5 Kinetics of ion exchange

As with all aspects of mass transfer, kinetics are very important. In most situations it is desirable to have very high kinetics though there are always limitations. The resistances to mass transfer in ion exchange may be summarised as follows:

- Diffusion of ions to a boundary layer surrounding the resin bead.
- Diffusion through the boundary layer to the resin bead surface.
- Diffusion through the pores of the resin bead.
- Slow exchange at the fixed site.

Similar resistances may also apply to ions diffusing out of the resin bead. Diffusional resistances in the boundary layer may be significant and depend on agitation or flowrates. Diffusion through the pores of the bead may also represent a significant resistance. The other two resistances are usually small and insignificant.

The following models have been used to describe ion exchange rate [1,10]:

1st order

$$Log_{10}\left(1-\frac{X}{X_I}\right)=kt \qquad . \quad . \quad . \quad . \quad . \qquad (1.5a)$$

Modified Freundlich

$$X = kC_O t^{\frac{1}{m}} \qquad . \quad . \quad . \quad . \quad . \quad . \qquad (1.5b)$$

Parabolic Diffusion

$$F = Rt^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1.5c)$$

Elovich

$$X_t = \left(\frac{1}{\beta}\right)\ln(\alpha\beta) + \left(\frac{1}{\beta}\right)\ln(t) \quad . \quad . \quad . \quad . \quad (1.5d)$$

X_t = Amount of NH_4^+ adsorbed at time t (mg/g)
X_0 = Amount of NH_4^+ adsorbed at equilibrium (mg/g)
t = Time (min)
C_0 = Initial NH_4^+ concentration (mg/l)
α,β,k,R = Constants

1.2.1.6 Ion exchange in zeolites

A zeolite is a 3-dimensional aluminosilicate consisting of AlO_4/SiO_4 tetrahedra, and cations [13]. Each aluminium or silicon tetrahedra is connected by shared oxygen atoms and therefore carries an overall negative charge, which is balanced by the cations. Due to the sharing of oxygen atoms the ratio of oxygen to Al+Si is two rather than four. The cations present in the zeolite depend on the cations present in the groundwater, and on the affinity of each site in the zeolite towards each cation.

The chemical formula is dependent on the central ion as it sets the charge, which is balanced by the number of cations present. A higher ratio of aluminium to silicon will require more cations, hence a higher capacity. There are a number of different

arrangements of the tetrahedrons and ratios of the Si_4^+ or Al_3^+ ions, which form different zeolites. Some zeolite groups are:

- Analcime
- Chabazite
- Gismondine
- Heulandite
- Natrolite
- Harmotome
- Stilbite

Within these and other groups are individual zeolites, each defined by the different structural possibilities of the zeolite framework. There are more than 40 known naturally occurring zeolite species. Zeolites are usually found in volcanic sites in such countries as Bulgaria, Hungary, Italy, Japan, New Zealand, and the USA [13,14,18].

Uses of zeolites include:

- Gas phase adsorption of CO_2 and H_2O
- Oil absorption for spills
- Fertiliser
- Catalysts in the petroleum industry
- Filler in paper
- Ion exchange (water softening, heavy metal removal, NH_4^+ removal)
- Kitty litter

Zeolites can form at either low or high temperatures. They form by the alteration of volcanic ash under beds of water, which trickles down through the ash. As the water trickles through, the pH changes and gives rise to layers of different zeolites. High temperature zeolites are formed in hydrothermal vents and may be formed much more rapidly due to the higher temperatures. Clinoptilolite can be found in either high or

low temperatures areas [13]. The tetrahedral building block can form all shapes of zeolitic crystals, see Figure 1.7.

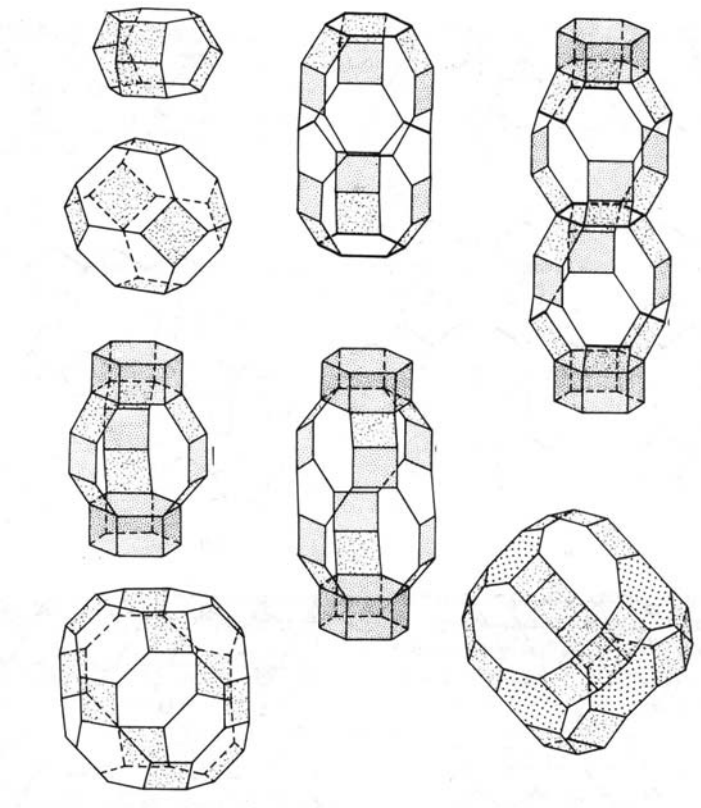


Figure 1.7: Various zeolitic structures [14].

Pores and sites

One of the most important features of zeolites of interest in ion exchange are the pores through which ions can diffuse. Diffusion can occur in 1-d, 2-d, or 3-dimensions. 1-dimensional diffusion occurs through pores, 2-dimensional between plates and 3-dimensional through open structures.

Figure 1.8 shows the structure of sodalite, it can be seen that the structure is open and porous. It also shows aluminium, silicon, oxygen and cationic sites.

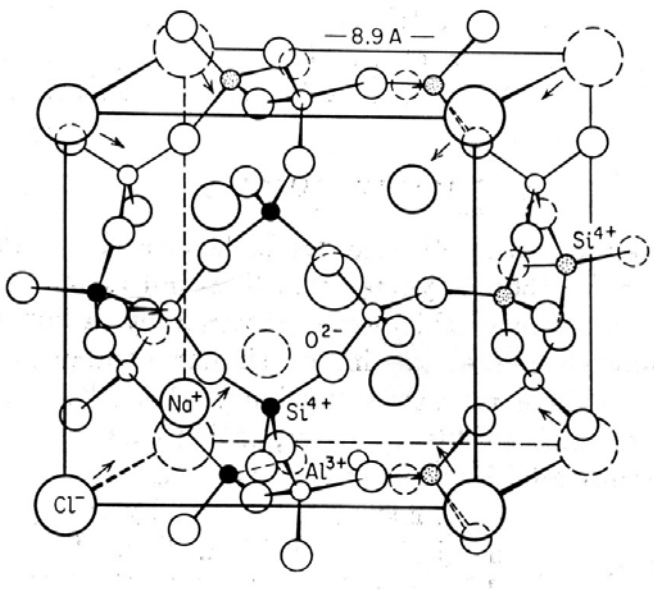


Figure 1.8: Crystalline structure of sodalite [1].

Different pore sizes, geometry, atoms, and water molecules can surround each of the anionic sites in the zeolitic structure. At each of these sites different cations are preferred over other cations (see section 1.2.1.6).

Clinoptilolite

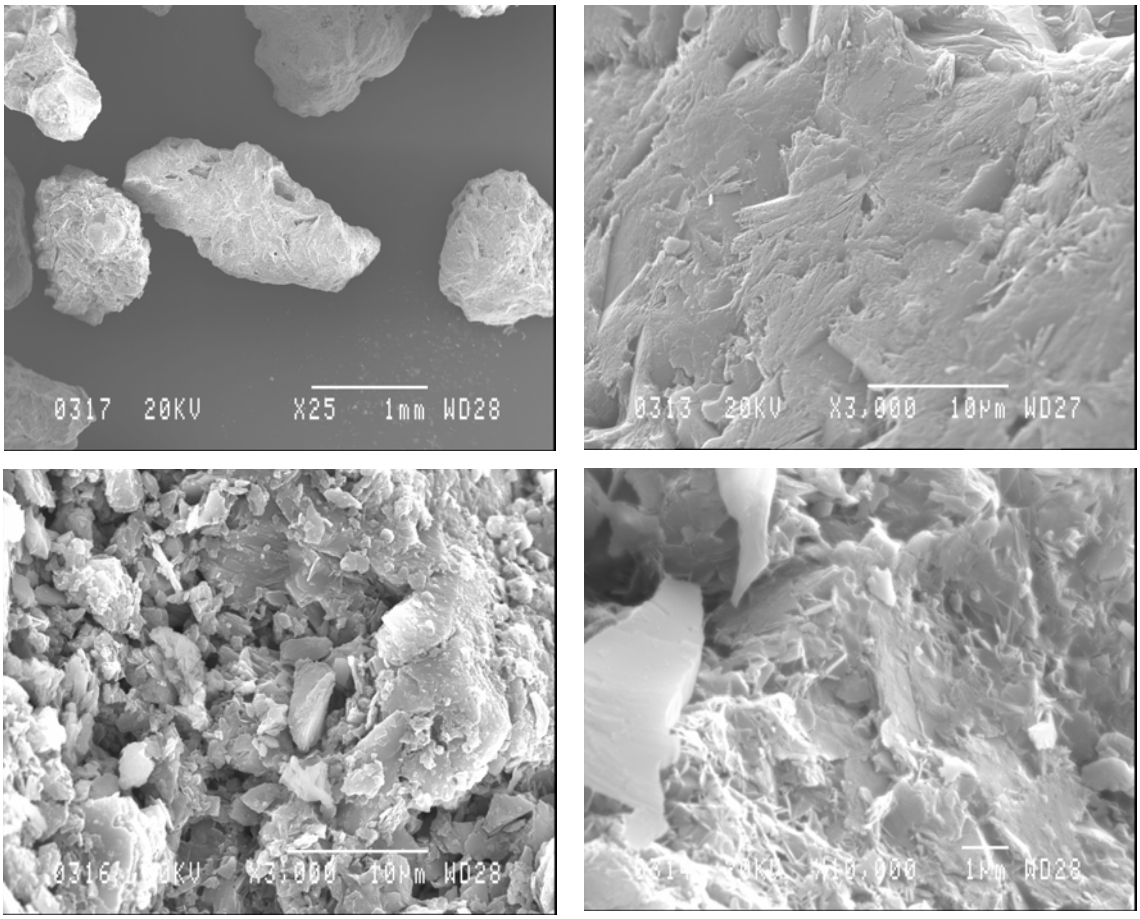


Figure 1.9: Scanning electron micrograph of clinoptilolite.

The particular ion exchanger of interest in this study is clinoptilolite, which is known to have a high affinity for ammonium ions [16,18,21,23,26-29,44,50]. Clinoptilolite is an abundant zeolite found in nature, and was once regarded as its own species until it was found that it was a silica-rich heulandite, with an ideal formula as follows:

$$Na_6Al_6Si_{30}O_{72}.24H_2O \quad . \quad . \quad . \quad . \quad . \quad (1.6)$$

The cations found in natural clinoptilolite are Na^{+}, Ca^{2+}, some K^{+}, Mg^{2+}, and traces of metals such as Fe^{3+}, Sr^{2+}, and Ba^{2+}. Clinoptilolite and other zeolites can contain large amount of impurities or other zeolite crystals. The clinoptilolite used in this work was 90% - 92% pure which is quite high.

The shared oxygen atoms between aluminium and silicon in clinoptilolite gives rise to a negative charge that is counter acted by the presence of sodium cations. The sodium ions are only held by their ionic forces, which make them exchangeable when other cations are present in solution. The more aluminium present the higher the capacity of the zeolite. Clinoptilolite is a silica-rich zeolite. Therefore it has a lower capacity than many other zeolites, though has a number of other properties such as a high selectivity for NH_4^{+} ions, and resistance to degradation by acidic solutions. Typical ammonium ion capacities for clinoptilolite are in the range of 32-40mg/g [50], or 31-38.5mg/g [16] (for clinoptilolite initially in the Na^{+} form).

Figure 1.10 shows the structure of clinoptilolite from two different authors.

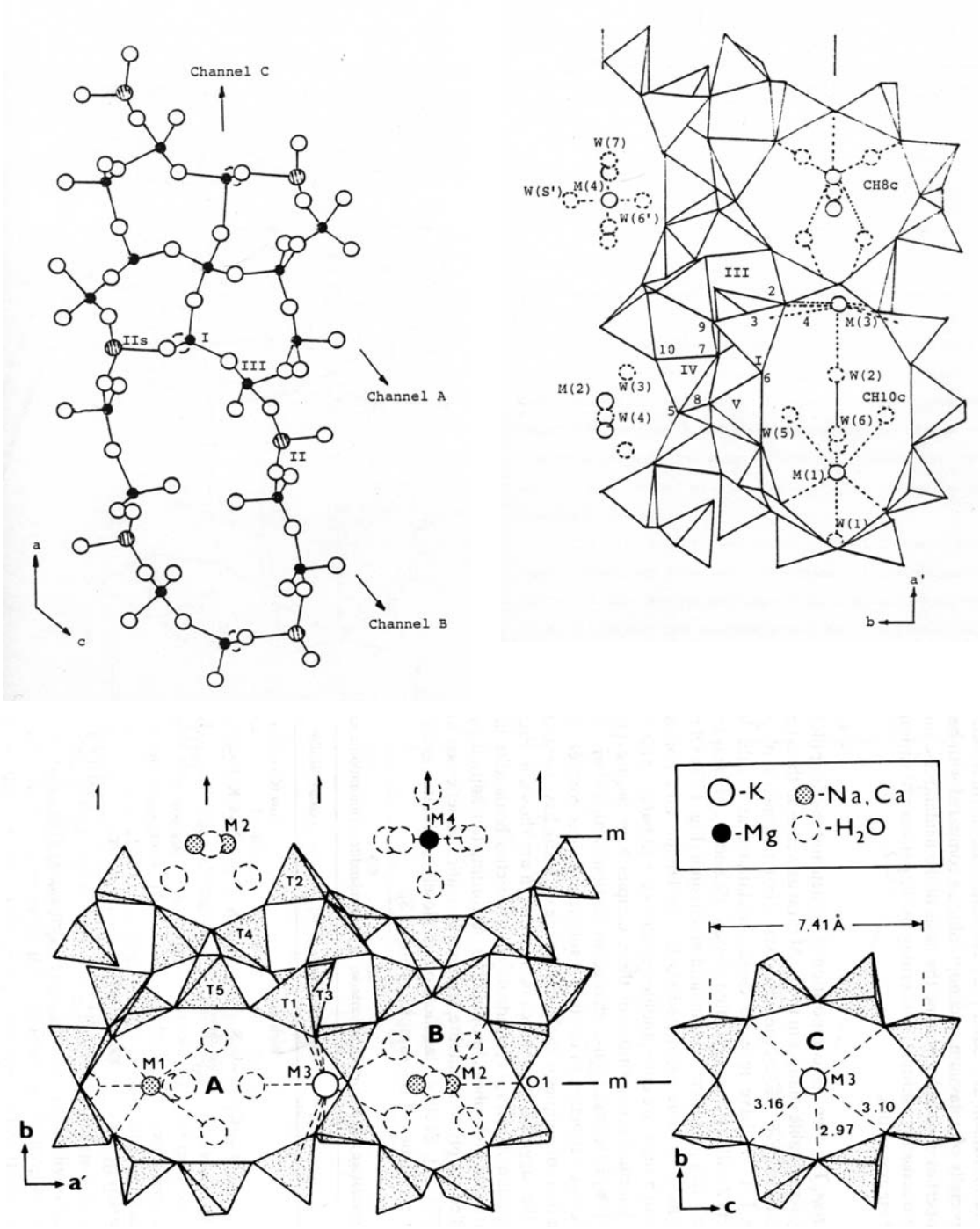


Figure 1.10: Crystalline structure of clinoptilolite. [14,16].

Studies of clinoptilolite [14,16] have shown that there are 4 anionic sites in the structure. These are labelled M1, M2, M3, and M4 (M2 and M4 are divalent sites). The M1 and M2 sites in natural clinoptilolite are usually occupied by Na^+ and Ca^{2+}, K^+ in M3, and

Mg^{2+} in M4. There are also sites that are occupied by water molecules and are labelled W1 – W7. The crystalline structure of clinoptilolite is described as a series of plates [13,16,18].

Selectivity and capacity of clinoptilolite

The general definition of selectivity was previously discussed in section 1.2.1.4. This section deals with clinoptilolite specifically and with cations of relevance in the context of water treatment.

The cationic composition of natural clinoptilolite is predominantly determined by ground water [18]. Though in different solutions of mixed cations it will prefer some ions to others.

$$Cs^+ > K^+ > NH_4^+ > Sr^{2+} > Na^+ > Ca^{2+} > Fe^{3+} > Al^{3+} > Mg^{2+} \quad . \quad (1.7) \quad [18]$$

Equation 1.7 shows that Cs^+, K^+, and Sr^{2+} cations are potentially a problem, in the context of ammonium ion removal, although the Cs^+, Sr^{2+} are usually rare. The other relevant cations, Ca^{2+}, Na^+, and Mg^{2+}, are likely to have an effect on ammonium uptake if present in reasonable quantities but previous research has shown that this is a small effect [16,18]. It is unlikely that clinoptilolite will find applications for removal of NH_4^+ from marine water as the capacity of a bed for ammonium uptake would be heavily negated by Na^+, and K^+ uptake.

Zeolites with a high Al/Si ratio (high charge density) prefer small, highly charged ions such as Ca^{2+}. High Si/Al ratio (low charge density) will favour lower charged ions

such as NH_4^+ and K^+ [18]. As can be seen from the selectivity order above, monovalent ions are preferred over the multivalent ions.

The pore dimensions may also influence the selectivity of clinoptilolite. The structure of zeolites is quite rigid and therefore they do not swell or shrink to any significant degree, which gives rise to their molecular sieve properties. This is different to low cross-linked polymer exchangers which can swell in the presence of larger cations.

Factors which may influence cation selectivity may be summarised as follows:

- Cation charge
- Diameter of cation, with and without water of hydration
- Cation hydration energy
- Concentration of species in the liquid phase, especially the electrolytes
- Temperature
- Structure and number of sites in the resin

Cation diameters represent an important parameter in selectivity. The hydration energy of the water molecules surrounding the cation is also important.

Table 1.1: Cation size and hydration energy [16].

	Ionic radius (A)	Hydrated radius (A)	Hydration energy (kJ/g)
K^+	1.33	5.3	394
NH_4^+	1.43	5.35	364
Na^+	0.95	7.9	477
Ca^{2+}	0.99	9.6	1717
Mg^{2+}	0.66	10.8	2051

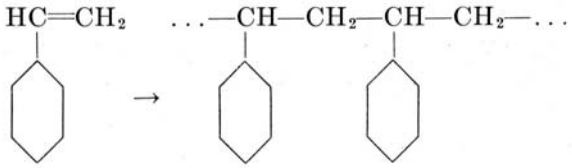
With the cations ordered in selectivity, from top to bottom, it can be seen that the preferred ions have a smaller hydrated ionic radius and lower hydration energy. Smaller ions are less prone to molecular sieve effects. A lower energy of hydration makes it easier for the zeolitic forces to overcome the hydration forces.

It was mentioned in section 1.2.1.6.2 that the capacity of clinoptilolite varied between 32 – 40 mg/l (31 – 38.5 meq/l). A previous study [16] found that the capacity was not the same for different cations. Initially resins were conditioned into various homoionic forms and each of these was contacted with other cations. Most cations exchanged to 100% of the total capacity. Mg^{2+} however only exchanged to ~20% of its total capacity. This was believed to be caused by Mg^{2+} only occupying the M4 site

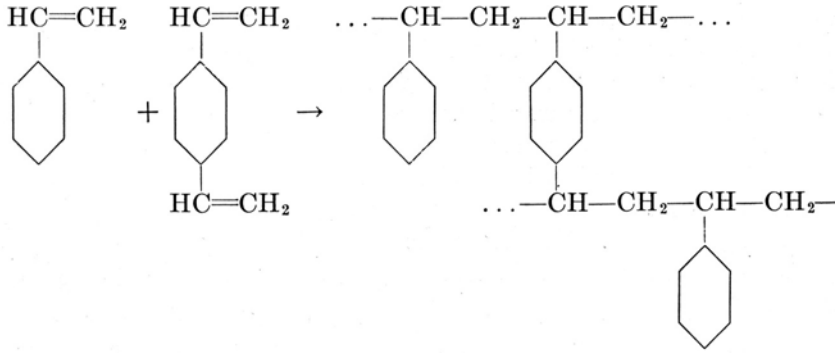
1.2.1.7 Polymeric ion exchangers

Zeolites, and clinoptilolite in particular, are useful ion exchangers due to their low cost, ease of disposal, and their high selectivity for NH_4^+. Because they are naturally occurring they were among some of the first exchangers used for large scale application. New technology however saw the introduction of polymers with functional groups that took part in ion exchange. There are only a limited number of zeolites that are useful as ion exchangers, yet many combinations of synthetic exchangers are possible.

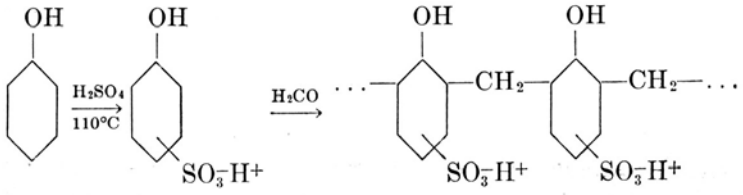
The first synthetic ion exchangers were prepared in the mid 1930's. There are many possible combinations of polymers, cross-linking, and functional groups. Monomeric organic electrolytes can be polymerised, or polymerisation can take place and functional groups added later. One of the most common polymers used for ion exchange resins is polystyrene cross-linked with divinylbenzene (a brief summary of the chemical synthesis can be seen in Figure 1.11).



Polymerisation of styrene to form polystyrene.



Polymerisation of styrene in the presence of divinylbenzene to form cross-linked polystyrene.



Sulphuric acid in the presence of aldehyde and high temperature, to form sulphonic acid functional groups.

Figure 1.11: Preparation of ion exchange resins.

Cationic: $-SO_3^-$ $-CO_2^-$ $-PO_3^{2-}$

Anionic: $-NH_3^+$ N^+ S^+

Figure 1.12: Common functional groups.

Polymeric ion exchangers have many practical applications. They have high capacity, high kinetics, and chemical and mechanical stability. Unlike polymeric exchanger resins zeolites are more stable at high temperatures, though applications for ion exchange at high temperatures are rare.

Functional groups may be attached to give the desired ion exchange properties for a particular application. Selectivity in particular may be controlled. For example the CO_2^- group is only ionic at high pH; at low pH it no longer functions as an ion exchanger. The NH_3^+ group is similar except it only functions at low pH. The strong acid or strong base sites work at nearly all pH ranges.

With zeolites the matrix is well structured, and it was shown that clinoptilolite has four types of sites M1, M2, M3, and M4 (see above). Polymeric resin matrices however are random, with random pores and sites in the structure. The matrix is also elastic and can shrink or swell depending on the cross-linking and the ions present, which determine the mobility of ions. A resin with a high degree of cross-linking is more rigid and less able to shrink or swell, and vice versa for a resin with very little cross-linking.

Dowex 50w-x8

Dowex 50w-x8 (the Dow Chemical Company) is an example of a polystyrene polymer cross-linked with divinylbenzene. The functional group is a strong acid, sulphonic acid type. It is a common cationic exchanger and has been in use for some time.

Purolite MN500

Purolite MN500 is an example of one of the more recent generation of ion exchangers based on macronet polymers, from Purolite. It was first developed in 1969 but the first commercial macronets were manufactured in 1993. High surface area is one of their main features; at 800-1100m^2/g. The macronets contain micropores (15A) that give them higher capacity, and macropores (800-950A) that have a low exchange capacity but allow for faster diffusion of ions through the bead. The large pores allow for easy cleaning during regeneration to remove species that would otherwise foul conventional polymeric exchangers [33].

Surface areas of other materials are:

- Clinoptilolite = 221.5m^2/g [18]
- Synthetic zeolites ≤ 500m^2/g
- Activated carbon ≈ 1050m^2/g

As can be seen the macronets have a comparable surface area to activated carbon.

Figure 1.13 shows a few grams of each exchanger resin (they are damp to hold them together). Clinoptilolite is a coarse sandy like material. The polymeric resins are small spherical beads.

Figure 1.13: Clinoptilolite, Dowex 50w-x8, Purolite MN500.

Figure 1.14 shows two scanning electron micrographs of the surface of Purolite MN500.

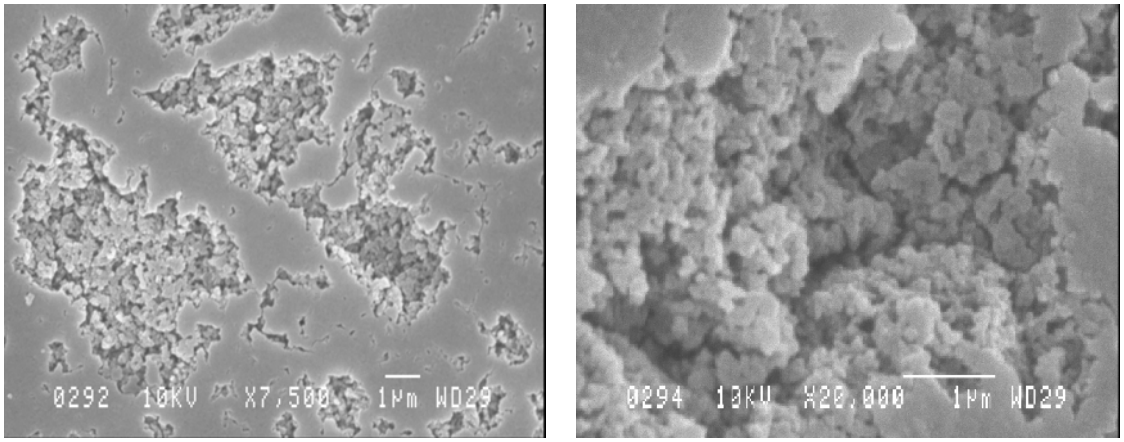
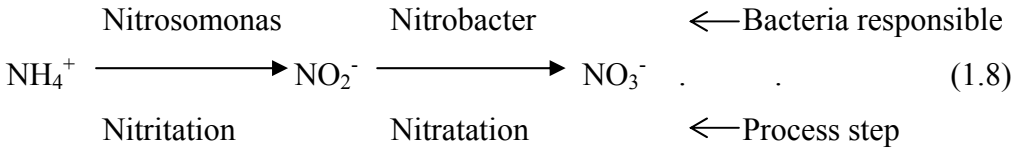


Figure 1.14: Scanning electron micrograph of Purolite MN500.

1.2.2 Biological nitrification

The traditional method for ammonia removal in water treatment processes has been that of biological nitrification. Nitrification is a two-step process carried out by two separate bacteria to convert NH_3 into NO_2^-, which is then converted into NO_3^-.



(1.8)

As can be seen ammonia is converted to nitrite by chemlithoautotrophic bacteria. Other nitrifiers include *Nitrosococcus, Nitrospira, and Nitrospina*. A number of different strains are responsible for the conversion within these groups. The two nitrifiers (Nitrosomonas and Nitrobacter) live in symbiosis and previous research [21] found that the two nitrifiers are not evenly mixed but form clusters with each other. Nitrifiers are often sourced from natural sources such as soil. Therefore in biological waste treatment systems mixed cultures are the major interest.

Nitrosomonas:

$$NH_4^+ + 1.5O_2 \Rightarrow NO_2 + H_2O + 2H^+ \quad (1.9a)$$

Nitrobacter:

$$NO_2^- + 0.5O_2 \Rightarrow NO_3^- \quad (1.9b)$$

Equations 1.9 show that large amounts of dissolved oxygen are consumed during nitrification (4.27g of O_2 per 1.0g of NH_4^+) [62]. Dissolved oxygen levels are commonly 8-10mg/l; therefore even small amounts of ammoniacal nitrogen can deplete oxygen levels. Oxygen levels can be replenished in a few different ways with

the most common being diffusion into waterways from air, especially with surface turbulence.

Previous research [62] has found that most of the NH_4^+ degraded is converted into nitrite and nitrate rather than more biomass. Heterotrophs have growth rates that are 10 – 20 times faster than the nitrifiers. Therefore with wastewaters that contain a mixture of ammonia and organic matter the heterotrophs compete strongly for nutrients and oxygen. Hence nitrifiers struggle to maintain such high numbers, if at all, in the mixed culture.

The optimum pH range for nitrification is reported at 7.0 – 8.5 [18,21], though observed rates are commonly better at the higher end of this range. At this pH most of the nitrogen is in ionised form (see Figure 1.1). This pH range is the optimum for the entire nitrification process, rather than each step. If the pH increases any higher too much NH_3 is present and inhibits nitrobacter. This may lead to a sudden build up of NO_2^-, which in turn inhibits nitrosomonas. At lower pH there is less free NH_3 available as a substrate. Without pH control or buffers nitrification rates drop off very quickly due to the production of HNO_2, and HNO_3.

The optimum temperature for nitrification is 30°C. Beyond this temperature dissolved oxygen levels can be substantially reduced and lead to a fall off in the rate of reaction. Nitrifiers also require an inorganic carbon source such as CO_3^- or HCO_3^-. The presence of CO_3^- and HCO_3^- ions tend to stabilise pH. Figure 1.12 shows the effects that a range of pH and temperature has on nitrification.

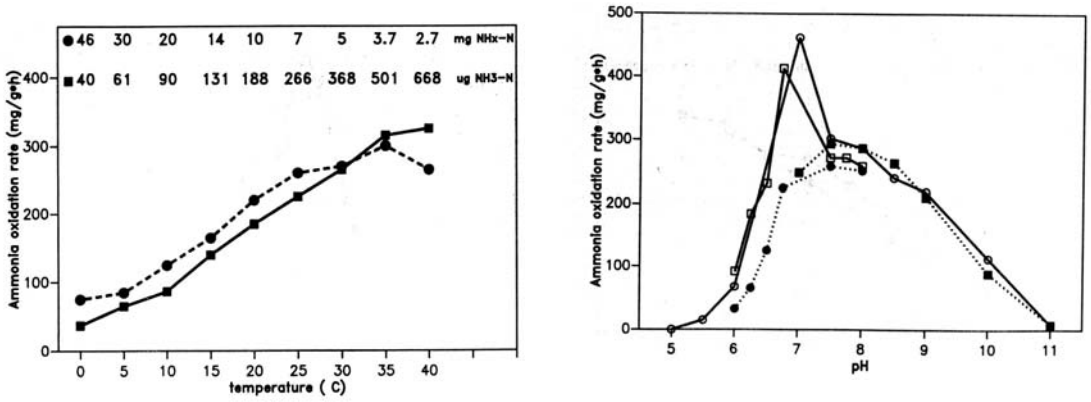


Figure 1.15: Effects of pH and temperature on nitrification [41].

Nitrate production (reaction 1.9(b)) usually occurs at a faster rate than nitrite production (reaction 1.9(a)), therefore NO_2^- concentrations are usually very low.

A previous research dissertation [21] found that a nitrifying colony preferred clinoptilolite rather than sand as its solid support. Possible reasons for this are clinoptilolite concentrates NH_4^+ near its surface. Clinoptilolite is also a mineral, therefore contains trace amounts of many nutrients that microorganisms require.

The products of nitrification are NO_3^- and small amounts of NO_2^-. Therefore nitrification may be coupled with a denitrification step to convert NO_3^- to gaseous forms of nitrogen (N_2, N_2O) [30].

Denitrification is carried out under strict anaerobic conditions. Nearly all denitrifiers are able to use NO_3^- or NO_2^- as electron acceptors. Denitrification usually occurs towards the end of a packed bed column as dissolved oxygen levels become depleted.

Denitrification: $NO_3^- \longrightarrow NO_2^- \longrightarrow N_2/N_2O$ . . (1.10)

To convert NH_4^+ to N_2 it is also possible to carry it out by shorter nitrification/denitrification. At high concentrations of NH_4^+ it is possible to inhibit nitrobacter, therefore the product of nitrification is NO_2^- [30]. NO_2^- can therefore be converted into N_2 without the two middle steps of:

$$NO_2^- \longrightarrow NO_3^- \longrightarrow NO_2^-$$

Some disadvantages of nitrification are as follows:

- Nitrifying bacteria only work well in a narrow temperature range, and hence the rate of removal significantly drops outside of the optimum.
- During nitrification HNO_3 is produced which can reduce the pH sharply, and thus reduce bacterial activity.
- The slow growth of nitrifiers means that they cannot adjust easily to peaks in influent concentration.
- During periods of antibacterial activity the removal capacity is lost.
- If organic pollutants are present heterotrophic bacteria will inhibit nitrifiers.
- Long start up periods may be required before the nitrification reaches full removal capacity.
- Nitrates in the discharge, especially at higher levels, can be of concern.

Advantages of nitrification are as follows:

- A cheap and continuous method of ammonia removal.
- Actually degrades the pollutant unlike ion exchange, which only concentrates pollutants by transferring it to another body of water.
- Technology is well established.

1.2.3 Combined ion exchange and nitrification

Ion exchange and biological nitrification, each have pros and cons as stand alone treatment processes. A novel approach would be to combine the two processes so that the advantages of both processes can be used simultaneously. Biological nitrification is the traditional method for ammonia removal but the problems associated with this method could be partially addressed by using ion exchange and nitrification together. As mentioned earlier biological nitrification cannot handle peaks or varying loads. A major downside of ion exchange is the cost of regeneration.

There are a number of different ways in which nitrification and ion exchange could be combined. Some possible combinations are as follows:

<u>In series:</u>

- Ion exchange upstream from biological treatment.
  The exchanger is not regenerated once loaded but smoothes out peaks and troughs to provide a near constant concentration to nitrifiers.
- Ion exchange downstream from biological treatment.
  Any ammonia passing through to the effluent is mopped up by the ion exchange resin. The exchanger resin will require regeneration once loaded.

<u>Combined:</u>

Rather than having the two stages separated they can also be combined in a single unit operation yet work in a similar way to that mentioned above.

- Biological treatment on the exchange resin.

Nitrifiers growing on the exchanger resin degrade the ammonia and are the primary removal method. However during periods of fluctuating concentration the exchanger resin is able to absorb and release ammonia in a controlled manner for the nitrifiers. A separate regeneration step of the ion exchange resin is not required.

- Clinoptilolite with the support of biological treatment.
  Clinoptilolite is the primary method of removal, however nitrifiers help extend bed life and also participate with biological regeneration.

1.2.4 Other removal methods

Other methods of ammonia removal include:

- Ozonisation, which is a highly reactive form of oxygen and converts ammonia to nitrate [2].
- Breakpoint chlorination, which also converts NH_4^+ to nitrate.
- Air stripping where at high pH NH_3 is stripped through a packed column with air or steam.
- Polymeric membranes exist that at highly selective towards NH_3 molecules.

1.3 ADSORPTION

Adsorption is another important unit operation used in water treatment and there are a number of differences and similarities when compared with ion exchange. Adsorption is when an adsorbate from a liquid or gaseous phase attaches itself to an interface. There are two types of adsorption, physisorption and chemisorption [9,20].

- Physisorption is when Van der Waals forces physically attract the adsorbate to the solid absorbent, overcoming the kinetic forces of the adsorbate in the liquid. This can result in either monolayer or multilayer adsorption.

- Chemisorption is when a product of a chemical reaction between the adsorbate and adsorbent resulting in a monolayer.

The selectivity of adsorption depends not only on the adsorbate and the absorbent but also the solvent. Just like ion exchange there are mechanisms which carry the adsorbate to the solid phase.

1. Bulk diffusion through the solvent.
2. Film diffusion through the boundary layer surrounding the particle.
3. Internal diffusion (a) diffusion through the pores and (b) site hopping where the adsorbate hops from one site to another.
4. Uptake of the adsorbate to the adsorption site.

Steps 2 and 3 are regarded as having the highest resistances to mass transfer.

There are a number of different adsorbents in use but the most common are activated carbon, metallic oxides, and zeolites. There are a number of different models for adsorption but the two most commonly applied are the Langmuir isotherm and the Freundlich isotherm. These two models relate liquid phase concentration to solid phase concentration for equilibrium processes [9,20].

Langmuir $$Q_e = \frac{a.C_e}{1+(b.C_e)} \quad . \quad . \quad . \quad . \quad . \quad (1.11a)$$

Freundlich $$Q_e = x(C_e)^y \quad . \quad . \quad . \quad . \quad . \quad (1.11b)$$

Where:

Q_e = Solid concentration of adsorbate on the adsorbent (mg/g).

C_e = Liquid concentration of adsorbate (mg/l).

a, b, x, y $\Rightarrow$ Constants for a specific combination of adsorbate/adsorbent/solvent.

The Langmuir and Freundlich isotherms can also be used to model ion exchange. The Langmuir isotherm has been found to be suitable for ion exchange, as some of the assumptions used in deriving it include the following:

- There are a fixed number of sites.
- Only one solute molecule per site

Both of these assumptions work well with ion exchange.

1.4 APPLICATIONS

Ammonia removal is a significant problem in a range of wastewater treatments. The municipal wastewater industry generates large volumes of ammonia contaminated water after primary and secondary treatment. The land based aquaculture industry and the oil refining industry also produce significant volumes of ammoniacal wastes. In all these cases reliable removal technologies believe a high standard of treated wastewater is required.

Clinoptilolite, or other cationic ion exchange resins, can be used to remove NH_4^+ from many aqueous situations. One area interested in ion exchange using clinoptilolite is

aquaculture, where the main competing technology is biological nitrification. Ammonia is a product of aquaculture; it is highly toxic to fish, even at very low concentrations.

Due to the increased use of water by industry, water resources are becoming depleted, especially in the United Kingdom and Europe. Therefore a large percentage of the water needs to be recycled (commonly 95%) [16]. Legal requirements are likely to mean that water must also be treated before it is released. Recirculation also allows for greater control of certain parameters, especially temperature, as introduced water can be of variable quality. Introduced water may contain other wastes, chemical run-off from farms or orchards, or pathogenic bacteria. Recirculation will however increase costs.

There are a number of other pollutants arising from aquaculture, though ammonia is one of the main problems. The unionised form (NH_3) is considerably more toxic than NH_4^+. A number of factors change the equilibrium such as, salinity, CO_2, temperature, though the most important is pH. Fish can acclimatise to moderate concentrations of NH_3, however fluctuating concentrations can have very serious affects on fish mortality. Common concentrations of NH_4^+ in aquaculture are 1 – 5mg/l [16].

An alternative NH_4^+ removal method is by ion exchange, particularly with the use of the low cost clinoptilolite with its high affinity for NH_4^+. NH_4^+ concentrations in aquaculture water are significantly lower than in municipal water; (1.0-5.0mg/l for aquaculture, up to 100mg/l for tertiary treatment of municipal water, and as high as 600-700mg/l for tertiary treatment of wool scour water) [7,16]. Therefore a column of clinoptilolite does not become exhausted as quickly. Ion exchange works by a totally different method to biological treatment and offers a number of different advantages:

- Low temperature sensitivity
- Ability to handle shock loads
- Very low concentrations of NH_4^+ in the effluent

- No start-up required
- Generally more reliable

Disadvantages however include:

- Higher capital and running costs
- Poor performance in saline or marine water

There are a number of other factors which require attention during the design of a system. Each type of fish species also requires specific conditions for optimal growth. A number of different stages are required for treatment before water is returned. One of the most important stages is however the NH_4^+ removal.

1.5 FOULING BY AMINES

Most ionic organics are anionic, and therefore do not participate in cationic ion exchange. There are however a few cationic organics, the most common of which are nitrogen based such as amines. Therefore the organic can participate in ion exchange.

A literature search revealed that there were a number of different important phenomena that occur in the presence of amines.

- Some amines have a higher affinity than NH_4^+ onto clinoptilolite [14].
- Not all amines can be taken up by clinoptilolite due to the size or shape (stearic hindrance), i.e. molecular sieve effects in the zeolite.
- The main difficulty however was the inability to regenerate the resin. Once certain amines were in the resin they could not be removed. A number of methods were tested to regenerate the resin including alkaline regeneration, biological regeneration and even thermal regeneration, each with no success.

The zeolites, after a few cycles, were then effectively poisoned and were of no further use [14].

To fully understand the effect amines and proteins would have on ion exchange would require comprehensive study and was not included in the scope of this project.

Due to the wide range of amines possible in wastewater each industrial site would need to investigate the effect of the amines to prevent permanent poisoning of the zeolite. If amines were found to be a problem pre-treatment would be required such as biological degradation or adsorption onto activated carbons.

2.0 PROJECT AIMS

2.1 OBJECTIVES

There are three mains objectives to the research conducted in this project:

1. To study the effects of organics on the behaviour of clinoptilolite.
2. To determine if ion exchangers could also take up organic pollutants by adsorption.
3. To evaluate new polymeric cationic resins for NH_4^+ removal from wastewaters.

2.1.1 Topics studied

- Initial characterisation of the clinoptilolite used.
- Measurement of the effect of organics on NH_4^+ ion exchange equilibria, onto clinoptilolite.
- Study of the adsorption of organics onto 3 exchanger resins and 2 adsorbents.
- Characterisation of two synthetic resins (Dowex 50w-x8, and Purolite MN500).
- Determination of the effects of organics on NH_4^+ ion exchange equilibria, onto Dowex 50w-x8, and on to Purolite MN500.
- Determination of the effect of organics on ion exchange in a column, and regeneration of each of the three cationic resins.
- Study of diffusion of ammonium ion through each of the three exchangers, in the presence of organics.

2.2 MOTIVATION FOR THE PROJECT

2.2.1 Effects of organics on clinoptilolite

A previous study [50] found that the removal of ammonium ions, by clinoptilolite, from piggery wastewaters was much less than from other waters. It was believed that this was due to the higher organic content in the piggery water than other sources. It was believed that small suspended solids could block pores, hence inhibiting the diffusion of NH_4^+ ions through the pores. It was also reported that the presence of organic matter might influence the surface charge density on zeolites.

Organic compounds can foul anionic resins because most ionic organics are anionic. Examples are fatty acids, which contain large anions which could exchange into the resin, and are difficult to remove. A small amount of literature [14] was found on amine fouling of zeolites and will be introduced later in this chapter.

The main motivation for the project was that despite the fact that organic pollutants are usually present with NH_4^+almost no literature could be found describing the effect of organic compounds on cationic exchange.

2.2.2 Adsorption

Another facet studied was the potential adsorptive capacity of clinoptilolite for the removal of organics from wastewater. Earlier work with clinoptilolite found that the uptake capacity, through adsorption, was very high. This suggested that clinoptilolite might also be an adsorbent to remove organic compounds from water, in addition to its ability to remove NH_4^+ ions.

2.2.3 Introduction of modern polymeric ion exchangers

Section 2.1 indicated that this work is a continuation of previous studies, on the use of clinoptilolite to remove NH_4^+. Nearly all the literature associated with NH_4^+ removal by ion exchange deals with clinoptilolite and in a few cases with mordenite. The most commonly used and modern ion exchangers however are polymeric. Therefore two polymeric exchangers were introduced into the area of NH_4^+ removal from water. The two polymeric resins are:

1. Dowex 50w-x8; a common cationic exchanger that has been available for many years.
2. Purolite MN500; a modern cationic exchanger, macronet range, from Purolite.

2.2.4 Kinetics

The rate at which most aqueous systems can be treated by ion exchange is dependant on mass transfer. There are a few resistances to mass transfer, though the most significant is diffusion through the resin bead. It is important to understand the kinetics of each of the three resins used, clinoptilolite, Dowex 50w-x8, and Purolite MN500, as achievement of fast kinetics will result in better column performance and higher utilisation of the exchanger. It is also possible that the presence of organic compounds may change the rate of NH_4^+ uptake, hence this was also studied.

3.0 MATERIALS & METHODS

3.1 PREPARATION OF CLINOPTILOLITE

The clinoptilolite (Dryden Aquaculture) was sourced from the Hector deposit in California. The mean particle diameter was in the range 2mm – 4mm. To reduce the particle size a Retsch BB 50 jaw crusher was used. Due to the brittle nature of the clinoptilolite, other high-speed grinders could not be used as they produced too many fines. After grinding, the clinoptilolite was added to Fritsch sieve shakers and classified. The classified clinoptilolite was then washed to remove any fines.

Previous work [18] used zeolite having particle diameters in the range from 500-710μm. At this size range too many fines were produced during grinding, so a size range of 500-1000μm was used. This range gave particles which could be used in a fixed bed system without exercising an excessive pressure drop, but at the same time did not provide excessive particle side diffusion resistance.

A magnetic stirrer was initially used for mixing the exchanger and solution during preconditioning, but the stirrer follower ground the clinoptilolite on the base of the conical flask giving substantial. Instead the clinoptilolite was soaked in the solution for 24 hours with regular agitation by hand. After this period, the solution was drained and the resin rinsed with distilled water. Fresh NaCl solution was added and the exchanger soaked overnight. This continued for a total of 7 days. The clinoptilolite was then washed with distilled water to remove excess NaCl and dried at 65°C overnight.

Preconditioning with acid or heat treatment was not employed as these methods change the structure. H^+ ions can remove impurities such as CO_3^{2-} from pores, but H^+ can also dealuminate the structure and cause a loss of capacity. Heat treatment can

reduce the affinity for NH_4^+ ions [16]. Alkali treatment is not believed to cause any structural changes.

3.2 ANALYSIS

3.2.1 Ammonia concentration determination

Two methods were employed to determine ammonia concentrations, namely, use of an ion-selective electrode, and secondly the classical Nesslerisation technique.

The first method made use of an ion selective electrode (Hach 50250, & Orion 95-12). The principle of operation is now briefly described. At the tip of the electrode is a hydrophobic membrane which is highly selective towards ammonia (NH_3) molecules. These diffuse from the sample solution, into the internal filling solution, until the partial pressure is the same on both sides. Ammonia then reacts with solution inside the internal filling solution to form ammonium and hydroxide ions. Inside the probe is a sensing element that is essentially a pH probe.

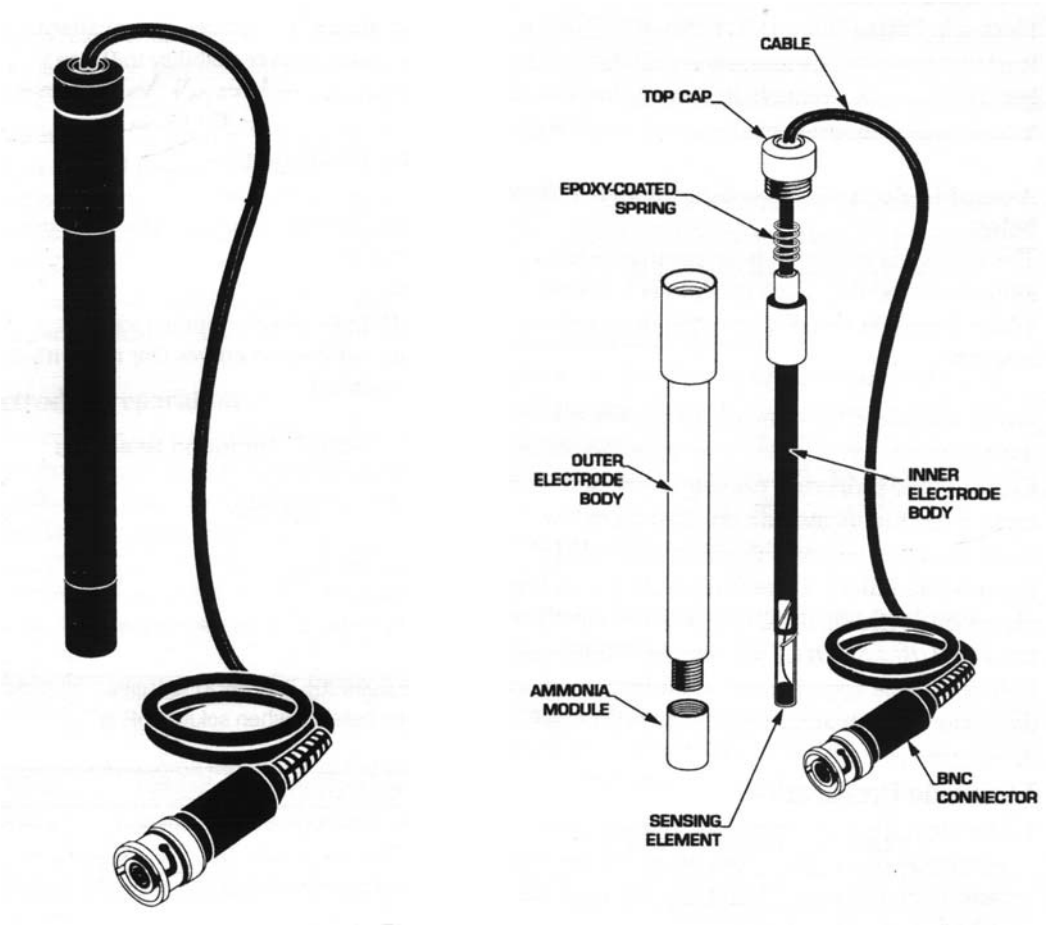


Figure 3.1: Hach 50250 & Orion 95-12 ammonia ion selective electrode.

Prior to use, the probe required calibration, twice as each sample is measured there was a slight change in the output reading from the electrode. For example if 20 samples of the same concentration were lined up it would be expected that a similar reading would be obtained for each. However as each sample was measured there was a slight drift in the reading. Therefore the calibration was made at the same time as the unknown samples were measured thus ensuring that the slight drift in readings was cancelled out.

For example, if there were 12 samples of unknown concentration, each would be lined up from lowest concentration to highest concentration. First a calibration sample with a concentration slightly below that of lowest unknown concentration was measured.

Then the unknown samples with the six lowest concentrations were measured. A second calibration sample would then be measured with a medium concentration. The final six unknowns would then be measured. Followed by the third and final calibration with a concentration slightly above the final unknown sample. The results of the calibration were plotted on a semi-log graph, and fitted with a logarithmic equation.

The membrane on the probe will only allow NH_3 to pass, so the pH was always at values greater than 11.5 (see Figure 1.1). A mixture of a pH indicator and lithium hydroxide was added to each sample. Neither the lithium hydroxide nor the pH indicator affected the electrode reading.

To determine if the different organics used in this research affected the measurement a number of ammonium solutions, each of the same NH_4^+ concentration and different organic concentrations were measured. They all gave the same reading. It can therefore be concluded that the presence of organics did not affect the analytical technique.

The ammonia probe was believed to give the best results in terms of accuracy, and precision. The membrane on the tip of the probe is highly selective towards NH_3 and there were no known interferences. The uncertainty for the probe was quoted as 2% for concentrations above 1mg/l (1ppm).

The second method used was the classical method for ammonia determination and employs a spectral method based on Nesslerisation [21]. A small amount of Nessler's reagent was added to each sample and forms a coloured complex with ammonia. The concentration of ammonia in the solution was determined by measuring the absorption in the visible region. Nessler's reagent compromises an aqueous solution of mercury (II) iodide, potassium iodide and sodium hydroxide.

A calibration curve was made using solutions of known concentration. Each sample was measured by mixing 25ml of the ammonium solution and 1ml of Nessler's

reagent (BDH). The mixture was then transferred into a 10mm quartz cuvette and its absorption measured in a Shimadzu MultiSpec 1500 scanning spectrophotometer four minutes after mixing. Depending on the range of concentrations to be measured, different wavelengths were used. The spectrophotometer was able to measure the entire UV and visible spectra within a two second timeframe. No particular wavelength was chosen for each analysis, rather all frequencies from 350nm – 600nm were measured each time. In this study Nesslerisation was only used as a check for the probe readings.

3.2.2 Chloride ion test

Chloride ion (Cl^-) concentration tests were carried titrametrically with silver nitrate ($AgNO_3$). A 20ml sample containing Cl^- ions was saturated with $NaHCO_3$, which was required to adjust the pH to 7 – 10. The 20ml sample was then added to a conical flask and 0.04g of Na_2CrO_4 added to act as an indicator. Na_2CrO_4 is initially a bright yellow colour. $AgNO_3$ (6.0g/l) was added and a precipitate of AgCl forms. Once all the Cl^- ions have precipitated, a precipitate of Ag_2CrO_4 begins to form, which has a brick red colour. The volume of $AgNO_3$ was recorded and the Cl^- concentration calculated by stoichiometry. This was also double-checked by titrating with known Cl^- ion concentrations. Blank analyses were also carried out in order to test the accuracy.

3.2.3 pH determination

Analyses for pH were carried out using a Hanna (HI1131) pH probe connected to a Hanna (pH211) meter. Calibrations were carried out using pH=4.01 and pH=7.01 buffers, resolution was to 0.01 pH units.

3.2.4 Temperature

Temperatures were determined with various mercury in glass thermometers.

3.2.5 Dissolved oxygen

Dissolved oxygen was monitored with a YSI 5739 probe attached to a YSI 58 O_2 meter. A two point calibration was carried out, 0 mg/l O_2, and saturated O_2 in deionised waterwater. The temperature was recorded to determine O_2 concentration at saturation. Resolution was to 0.1mg/l.

3.2.6 Protein analysis

Protein concentrations were determined using a protein kit supplied by Sigma. The method is based on a modified Lowry procedure. 2.0ml of protein solution was mixed with 2.0ml of Lowry Reagent Solution, which then stood for 20 minutes. Then 1.0ml of Folin and Coicalteu's Phenol Reagent Working Solution was added, which then stood for 30 minutes. The samples were then transferred to a quartz cuvette and the absorbance was measured between 500nm - 800nm. Calibrations were carried out with concentrations, 0mg/l – 400mg/l of protein standard (bovine serum albumin).

3.2.7 Nitrite/Nitrate analysis

Nitrite and nitrate concentrations did not need to be accurately determined, just whether they were present or not. A Hach NO_2^-/NO_3^- test kit was used with a number

of white strips and were used in a similar manner to litmus paper for pH testing. Each strip was placed in the solution for approximately one second then removed. If either NO_2^- or NO_3^- were present a strong pink colour would develop in 30 seconds. The concentration could be approximately determined from the intensity of the colour and the chart supplied with the kit. Concentrations as low as 0.1ppm could be determined.

3.3 EXPERIMENTAL

All experiments were carried out at 20°C ± 1°C.

3.3.1 Ion exchange, Batch studies

Three different ion exchangers were studied:

- Clinoptilolite (500μm-1000μm)
- Dowex 50w-x8 (290μm -840μm)
- Purolite MN500 (290μm -840μm)

Ion exchange equilibration measurements were carried out by contacting 0.8g of resin and 80ml of solution into a sealed bottle. NH_4^+ solutions were made using NH_4Cl. If a solution of 1000mg/l of NH_4^+ was required then 2965mg of NH_4Cl was weighed and made up to 1 litre. Organics were also added as required. Each bottle and other glassware was thoroughly cleaned and washed in distilled water.

Each sample was gently agitated by hand 4 times per day. Clinoptilolite is a brittle exchanger, and mixing could not be carried out mechanically. The time required for

equilibration was determined in a preliminary set of experiments. Equilibrium times were:

- Clinoptilolite = 4 days
- Dowex 50w-x8 = 5 days
- Purolite MN500 = 4 days

After 6 or 7 days each sample was filtered to remove any fines and placed in a 25ml sample bottle. Resin fines were removed so as not to interfere with the analysis and cause the reading to be higher than it should be. The addition of lithium hydroxide would release NH_4^+, increasing the ammonia concentration and would give a false reading.

3.3.1.1 Batch adsorption of woolscour water

There are many different wastewaters that require treatment before disposal. One such example is the tertiary treatment of woolscour water to remove residual COD and NH_4^+.

Woolscour wastewater is the product of washing grease and dirt from woollen fleece. Primary and secondary treatments include solids removal and biological treatment to lower the BOD. A number of compounds are not easily biodegraded hence the need for tertiary treatment. NH_4^+ is produced in the biological breakdown of proteins in secondary treatment.

Examples of compounds found in woolscour wastewater after secondary treatment:

- Ammonia
- Detergents

- Fatty acids
- Chlorinated hydrocarbons
- Phenols
- Plus a few others

The sample of wastewater used for these experiments had a NH_4^+ concentration of 576mg/l. This concentration is far too high to be treated by ion exchange in industry and would initially require other methods of removal.

As there was only one NH_4^+ concentration the amount of solid exchanger resin was varied to produce an isotherm.

Results of all equilibria were modelled by fitting either the Langmuir isotherm or the Fruendlich isotherm to the experimental data.

3.3.2 Organics adsorption, Batch studies

Batch adsorption studies were carried out using a similar technique to that used in the ion exchange experiments. 20ml of solution were contacted with 0.15grams of the solid resin. Four days were allowed for equilibrium prior to analysis.

Five different adsorbents were studied:

- Clinoptilolite (500μm-1000μm)
- Advanced filtration media (AFM) (500μm-1000μm)
- Dowex 50w-x8 (290μm -840μm)
- Purolite MN500 (290μm -840μm)
- Activated carbon (450μm -840μm)

Clinoptilolite, Dowex 50w-x8, and Purolite MN500 are the three ion exchange resins previously mentioned. AFM and activated carbon are two adsorbents used as a comparison. AFM (Dryden Aquaculture) is crushed soda glass. Activated carbon was supplied by Aldrich.

Three compounds were studied:

- Phenol – 0.235g/l (0.0025mol/l)
- Benzoic acid – 0.305g/l (0.0025mol/l)
- Whey protein – 0.40g/l

The pH was adjusted by addition of either HCl or NaOH. Only one concentration of each organic was studied, i.e. no isotherms were studied. Results were plotted in the form of a 3-dimensional bar graph as percentage of organic removed. Each combination was tested twice to check accuracy.

3.3.2.1 Preparation of resin for adsorption

Due to the presence of ions in solution, both ion exchange an adsorption will occur. To eliminate the effects of ion exchange occurring during adsorption, the three ion exchange resins clinoptilolite, Dowex50w-x8, and Purolite MN500 were preconditioned into different cationic forms. AFM and activated carbon are not ion exchangers, hence preconditioning was not required.

For acid exchange experiments (pH = 3.0) the resins were preconditioned into H^+ ionic forms, as were the resins used in the phenol and benzoic acid experiments with an unadjusted pH. The resins used with whey protein, with an unadjusted pH, and those used in all alkaline solution experiments were preconditioned into the Na^+ ionic form.

Therefore the resin and solution contained the same ions so that no net ion exchange occurred during adsorption.

It was assumed that the different ionic forms of the resins would not affect adsorption.

3.3.2.2 Analysis of organics for adsorption

Phenol and benzoic acid were analysed by UV spectrophotometry (Shimadzu 1500 multispec). Calibration curves were prepared from solutions of known concentration. Calibrations solutions were prepared at the same pH as those to be analysed. Absorption at wavelengths in the range 190nm – 340nm were measured. Whey protein was analysed as described earlier (see section 3.2.6).

3.3.3 Column studies

Image 3.2 and Figure 3.3 show a detailed diagram of the column and the four sample points through the column. The columns were made from Perspex tubing with dimensions shown in Figure 3.3

Image 3.4 and Figure 3.5 show a detailed picture of the septum and sample point. A thread was cut into the inside of the sample points and the opposite thread onto bolts. A silicon rubber septum was placed inside the sample point, up against a hole drilled into the column. A bolt with a hole drilled through it held the septum in place. Samples were taken by inserting a syringe into the sample point and withdrawing 25ml of solution.

The end of the column was considered as the 4^{th} sample point even though the resin was packed a little higher than this point.

Figure 3.2: Ion exchange columns.

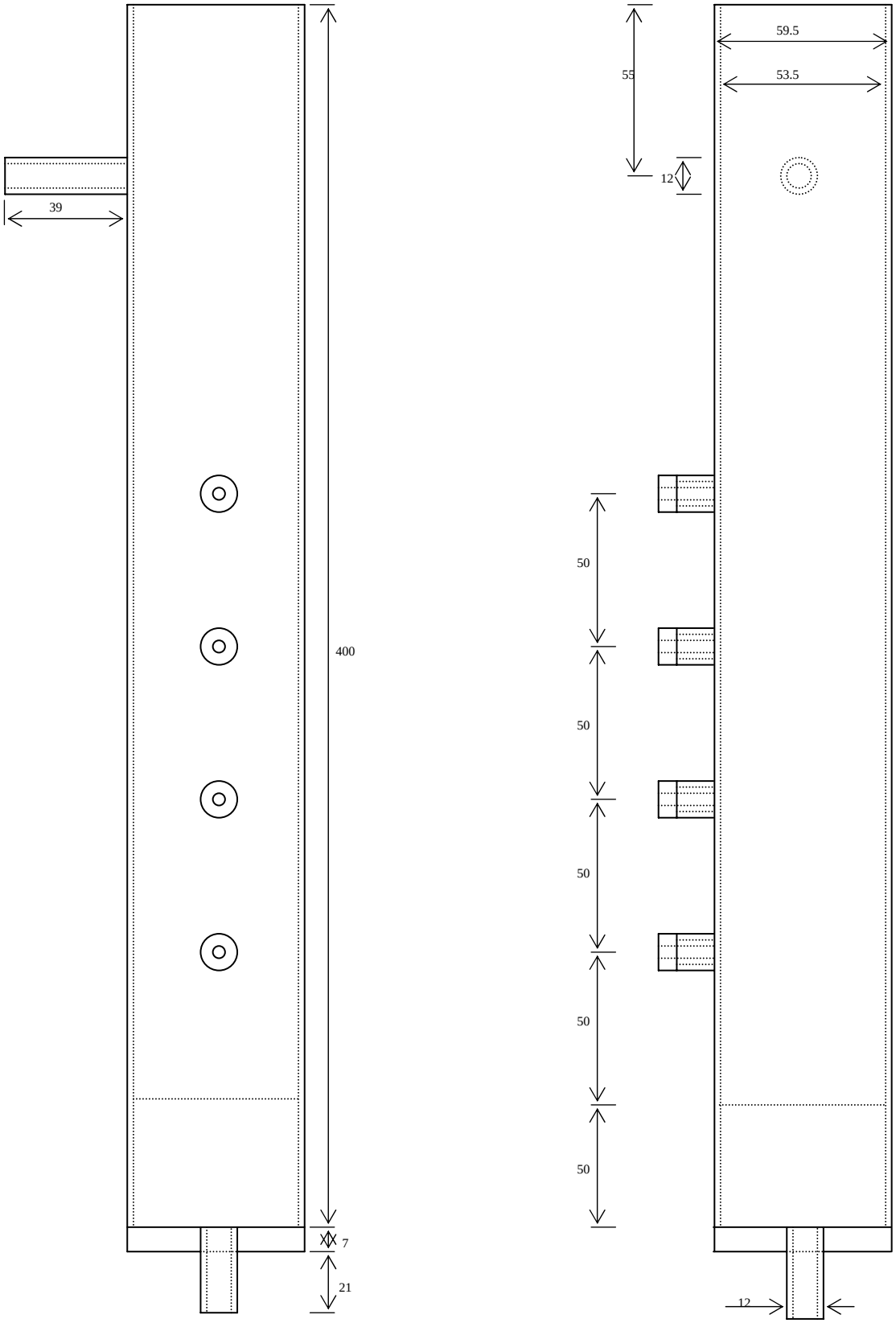


Figure 3.3: Column design and dimensions.

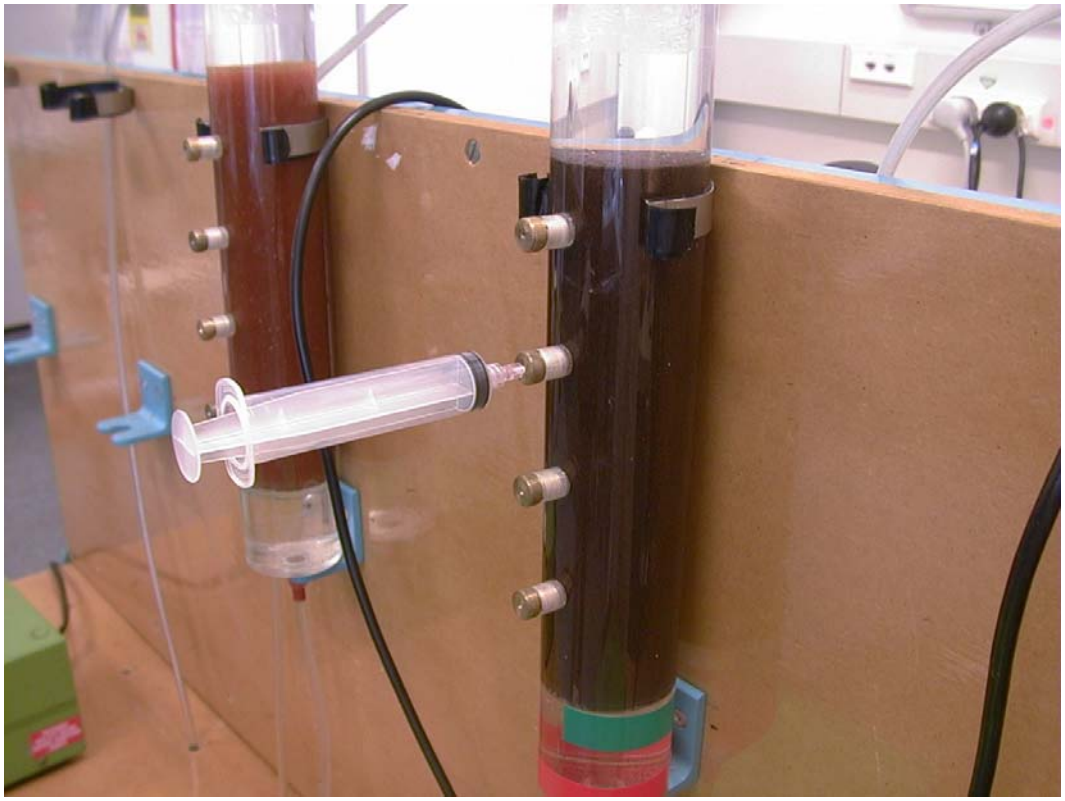


Figure 3.4: Column sample point.

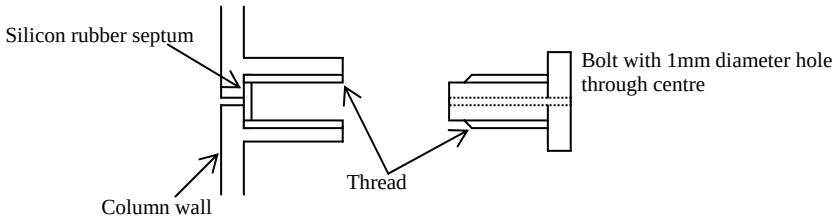


Figure 3.5: Sample point and septum design (exploded view).

There were four sample points on each column so that samples could be taken from inside the column. Between the tip of the bolt and the outside of the column wall was a silicon rubber septum to prevent water from escaping. A hypodermic syringe was used for sampling.

3.3.3.1 Preconditioning

Prior to fresh resin being used it was conditioned in a number of batch steps as described in section 3.1. Once in the column it was then preconditioned the same way that regeneration was carried out.

3.3.3.2 Regeneration of clinoptilolite

Once a column was loaded with NH_4^+ ions the feed solution was stopped. The column was then washed with 6 bed volumes (bv) of deionised water at 3bv/hr. 15bv of a regenerant solution (10g/l NaCl and 2.0g/l NaOH) was then pumped through at 1.5bv/hr. This was followed by 5bv of 2.0g/l sodium metabisulphite ($Na_2S_2O_7$) at 1bv/hr. The final stage consisted of 10bv of 10g/l NaCl and 2.0g/l NaOH at 2bv/hr. The regenerant solution was washed out with 6bv of deionised water at 3bv/hr. The column was then returned to service. (NB. A bv is the empty bed volume, 0.454 litres for this study).

The very alkaline conditions are likely to sterilise the clinoptilolite that may have developed during the service cycle, thus killing any biomass present. The middle step of sodium metabisulphite addition was also included just to be sure that full sterilisation took place during regeneration. The sodium ions present also helped with regeneration. It is unlikely that sodium metabisulphite would be included in an industrial scale process, due to the increased cost.

3.3.3.3 Regeneration of Dowex 50w-x8

The regeneration of Dowex 50w-x8 was very similar to clinoptilolite with the following sequence:

- 10g/l NaCl and 2.0g/l NaOH, 15bv at 1.5bv/hr
- 2.0g/l $Na_2S_2O_7$, 5.0bv at 1.0bv/hr
- 10g/l NaCl and 2.0g/l NaOH, 15bv at 2.0bv/hr

Slightly different volumes of regenerant solution were used due to the different capacities of each resin.

3.3.3.4 Regeneration of Purolite MN500

The regeneration of Purolite MN500 was very similar to clinoptilolite with the following sequence:

- 10g/l NaCl and 2.0g/l NaOH, 10bv at 1.5bv/hr
- 2.0g/l $Na_2S_2O_7$, 5.0bv at 1.0bv/hr
- 10g/l NaCl and 2.0g/l NaOH, 10bv at 2.0bv/hr

3.3.3.5 Service cycles

Before each experimental run all tanks, tubing and containers were sterilised with sodium metabisulphite (2.0g/l, BDH GPR grade), or household bleach to prevent biological contamination. The air supply to the lab was filtered to lower the risk of microbial contamination, however complete sterility could not be assumed.

Solution from a 25l feed tank passed through a Watson-Marlow peristaltic pump and then upflow (to minimise channelling) through the column. Once through the resin the solution continued to rise, then overflow down a drain. The flowrate for all the experimental runs was 3 bv/hr (1.36 litres/hr).

The columns and lab room were maintained at 20°C. To prevent dissolved O_2 from forming bubbles in the tubing, solutions were warmed to 22°C - 24°C in a water bath before they were added into the feed tank. The solutions then cooled to 20°C in the tubing prior to entering the column. Any gas bubbles that did get trapped in the entrance of the column were removed by a syringe through small sealed holes in the side of the column.

Distilled water was pumped into the column prior to resin being added. The resin was then added as a wet slurry. This was to prevent air bubbles from being trapped between particles, hence causing poor contacting in the column during each cycle. Between each service cycle and regeneration the resin was removed and repacked to ensure the resin bed was evenly packed for good distribution.

Solution was regularly added to the feed tank in 5L units. NH_4^+ concentrations were always 50mg/l (148.3mg/l of NH_4Cl).

Samples of solution were withdrawn at the same rate as solution was being pumped into the column. This was to avoid any unwanted back flow induced by the sampling procedure.

Samples were filtered through (ammonia free) Whatman filter paper into 25ml sample bottles. The filter paper did not contaminate the solution with ammonia and this was checked by soaking the filter paper in distilled water and testing for ammonia after a couple of minutes. Each sample was then analysed using the ammonia probe.

The overflow was regularly checked to determine if the correct flowrate was being used.

The volume of water treated was determined by recording the exact volume added and subtracting the volume of solution left in the feed tank and the one bed volume still present in the column. This was double checked by multiplying the flowrate by the processing time.

3.3.4 Kinetic studies

The two main resistances to mass transfer in ion exchange are the boundary layer surrounding each resin particle and diffusion through the resin particle. In highly agitated systems the boundary layer likely to be very small, leaving diffusion through the resin particle as the significant resistance.

The simplest way to reduce the boundary layer is to mix loose resin and solution with an overhead stirrer. Clinoptilolite is a brittle material; hence this method was not suitable. Therefore a design was developed where the water would pass very quickly over the resin.

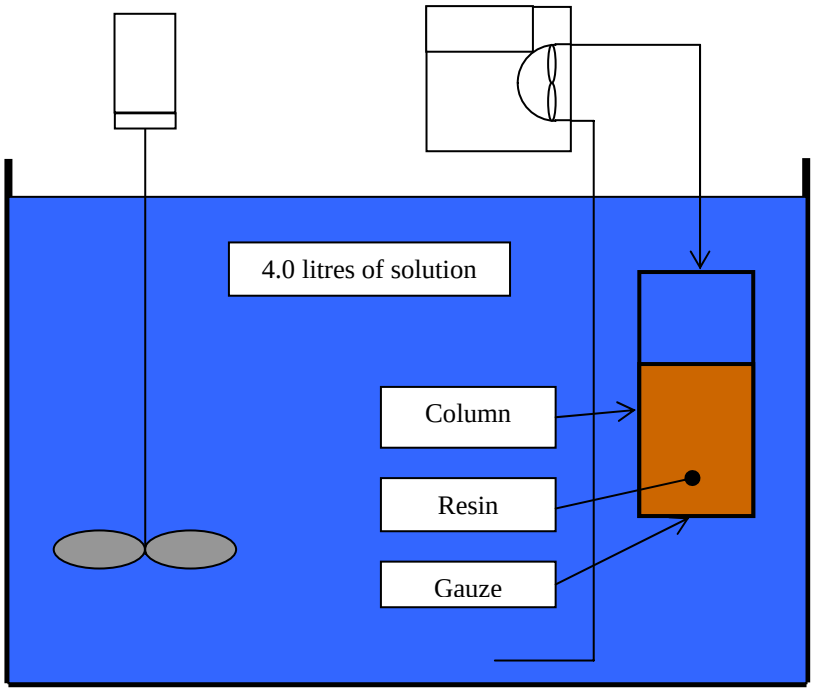


Figure 3.6: Kinetics equipment design.

The equipment used in the measurement of diffusion kinetics can be seen in figure 3.6. 4L of solution was held within a plastic container. An overhead stirrer at high speed kept the solution fully mixed. A short column (25mm diameter) with fine wire gauze attached to the base was used and into which 33.33g of ion exchange resin were placed. A peristaltic pump was used to recirculate solution very quickly through the column, therefore removing boundary layer effects. The tubing (10mm diameter) downstream of the pump and at the top of the column were sealed to ensure that all the flow went through the resin and out the bottom of the column.

A number of pump speeds were trialled. It was found that by running the pump over 40RPM the time taken to reach equilibrium remained constant. A pump speed of 80RPM was therefore adopted.

Due to the very high flowrates through the column the equipment does not behave like a normal column with a breakthrough curve. Solution took approximately 10 seconds to pass through the tubing and the column.

4.0 BATCH STUDIES, RESULTS & DISCUSSION

4.1 BATCH STUDIES ON CLINOPTILOLITE

4.1.1 Characterisation of clinoptilolite

Figure 4.1 shows the equilibria of NH_4^+ onto clinoptilolite in the Na^+ form. The experiment was carried out by a batch test as explained in chapter 3.0. Initial concentrations varied from 20mg/l – 1,000mg/l (NH_4^+). The final concentrations were measured after 6 days, and these can be seen on the x-axis. Experiments with starting concentrations of 1000mg/l of NH_4^+ showed a reduction in concentration, typically down to 750mg/l. The solid concentration (y-axis, mg of NH_4^+ per gram of clinoptilolite) was calculated from the decrease in liquid concentration and the amount of clinoptilolite added at the start. It was assumed that all NH_4^+ lost from solution exchanged with Na^+ ions onto clinoptilolite.

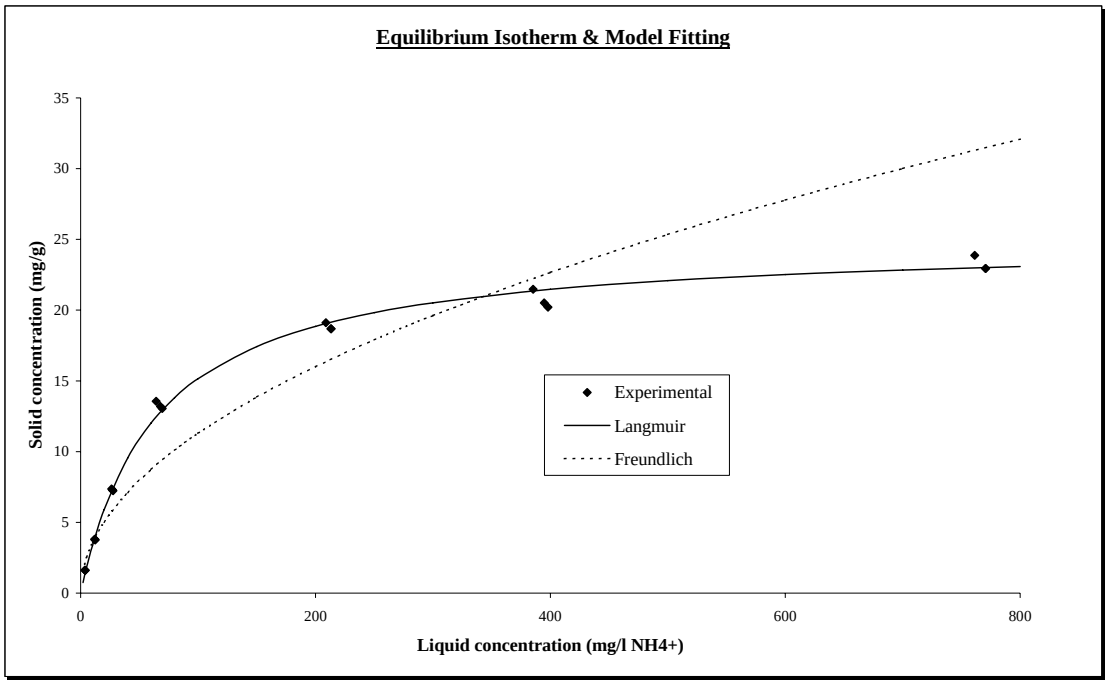


Figure 4.1: Equilibrium of NH_4^+ onto clinoptilolite.

[N.B. The y-axis has the units mg/g. This refers to milligrams of NH_4^+ ions taken up per gram of clinoptilolite in the original Na^+ form, not clinoptilolite in the H^+ form used by some authors].

As can be seen the Langmuir isotherm provided a very good fit to the experimental data. The Fruendlich isotherm provided a very poor fit. The results obtained agree with some of the assumptions made in deriving each of the models. The Langmuir isotherm assumes that there are a fixed number of sites and that each site can only hold one molecule from the solution. Whereas the Fruendlich isotherm assumes that there are an infinite number of sites. An ion exchange resin only has a fixed number of exchangeable sites and only one ion per site is permissible due to charge balancing. It is therefore no surprise that the Langmuir isotherm model fits the experimental data well.

The maximum uptake, according to the Langmuir isotherm, is 24.9mg of NH_4^+ per gram of clinoptilolite. Previous studies have found capacities of 32-40mg/g [50], or 31-38.5mg/g [16]. Using equation 1.4 the maximum theoretical capacity is 39.6mg of NH_4^+ per gram of clinoptilolite (assuming every Na^+ is exchanged for a NH_4^+ ion). Therefore the capacity found experimentally is 62.9% of the theoretical maximum value. Possible reasons for it being less than 100% are:

- Not all sites are accessible
- Inert material is included in the weight of resin
- Other zeolite structures might also be present
- Water of hydration may be different
- Preconditioning was not complete

Clinoptilolite is a naturally occurring ion exchange resin and therefore is likely to be of variable composition. From Figure 4.2 the prominent feature is that clinoptilolite from California showed a much larger uptake than the one New Zealand source. This could be due to varying quality, but more likely the processing to remove inert material and preconditioning produced a homoionic exchanger in the sodium form.

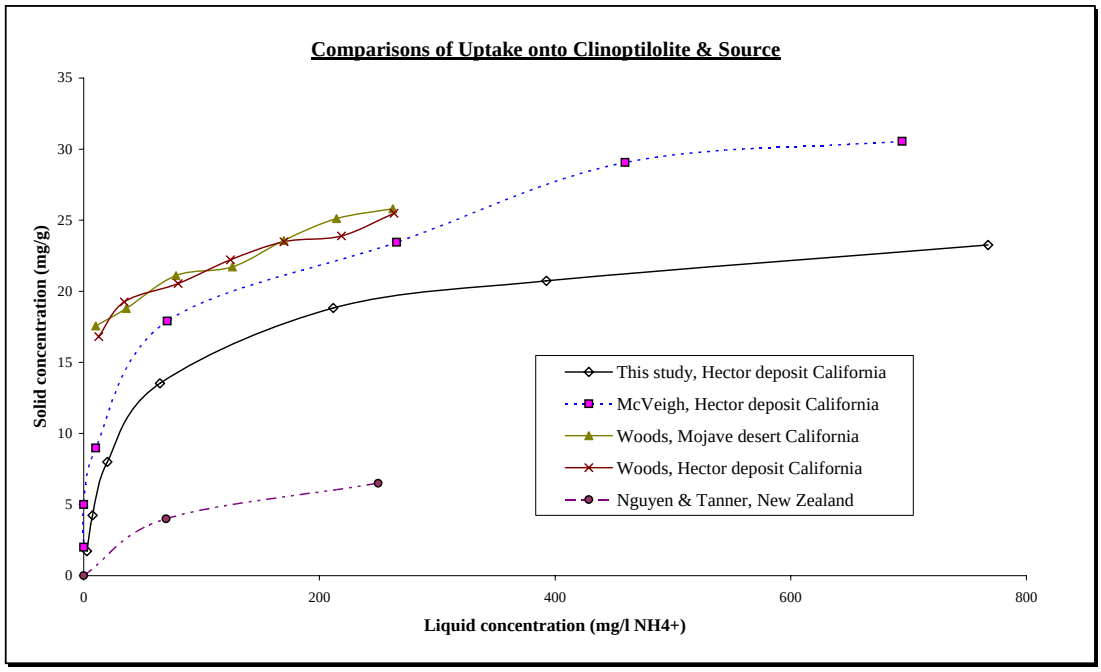


Figure 4.2: Comparison of different equilibria.

The clinoptilolite from this work and the clinoptilolite used by McVeigh were from the same source and both were preconditioned in a similar manner. The main difference though was that the clinoptilolite in this work was ground and classified. McVeigh only classified the clinoptilolite. The grinding process may have caused the pores to collapse, blocking off some sites from possible exchange, hence the slight difference in capacity. This has been observed in the adsorption behaviour of activated carbon [20].

4.1.2 Equilibrium of NH_4^+ in the presence of *simple* organics, onto clinoptilolite

The following section of work describes determination of a similar isotherm, as that shown in figure 4.1, was repeated in the presence of an organic compound.

N.B. The "NH_4^+-only" curve shown in the following figures is the Langmuir isotherm from Figure 4.1.

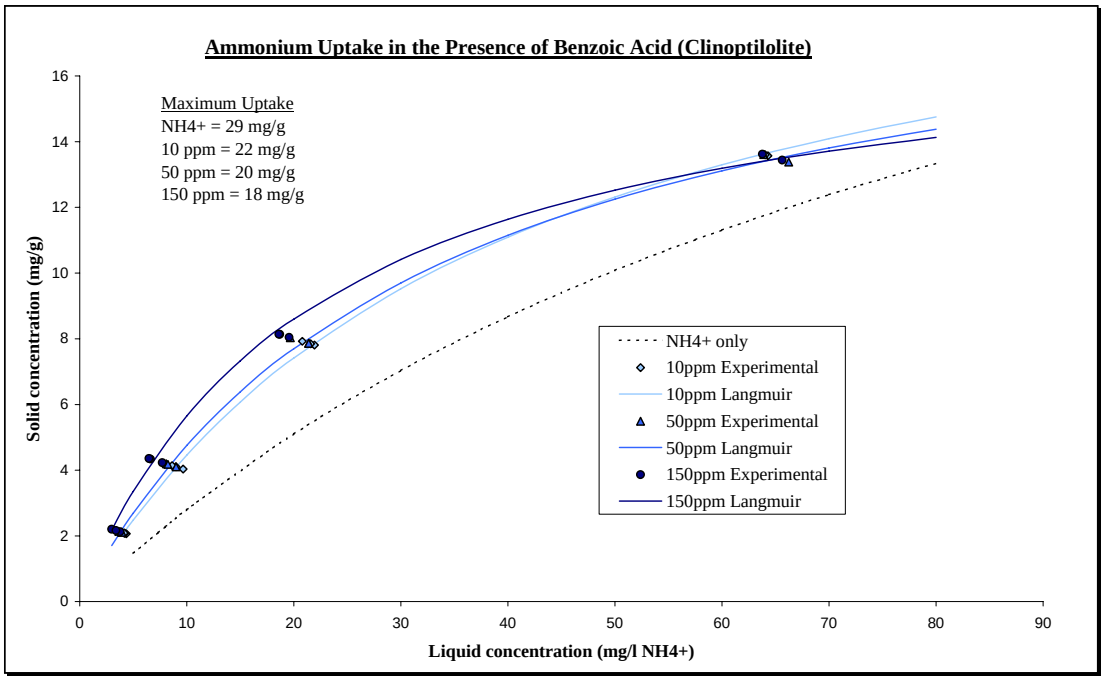


Figure 4.3: NH_4^+ equilibrium in the presence of benzoic acid, onto clinoptilolite.

Initial NH_4^+ concentrations were from 25mg/l – 200mg/l (74.1mg/l – 593.1mg/l of NH_4Cl). The same experiment was then repeated with fresh solution and clinoptilolite, although this time it was repeated in the presence of benzoic acid. Benzoic acid concentrations were 10ppm, 50ppm and, 150ppm (molar concentrations). Benzoic acid concentrations were not measured when obtaining the data for Figure 4.3; only the NH_4^+ concentrations were measured. Benzoic acid was added to see what effect its presence had on NH_4^+ equilibria.

It was initially expected that the H^+ ions present from the benzoic acid would compete for some of the ion exchange sites, and that the organic part of the molecule could foul or block other sites from ion exchange. Hence the NH_4^+ uptake should decrease as the

organic concentration increased. As can be seen from Figure 4.3 this is not the case and the data points for the 10ppm benzoic acid case are above those for "NH_4^+-only". There is also an increasing trend from 10ppm - 50ppm - 150ppm, although it is not as large as 0ppm - 10ppm.

Reasons for this enhancement are not fully understood, although some possible explanations have been ruled out. It is well known that nitrifying bacteria can colonise clinoptilolite [21]. In calculating the solid concentration values in Figure 4.3 it was assumed that all of the NH_4^+ ions which were removed from solution are exchanged onto clinoptilolite. If nitrifying bacteria were present then the NH_4^+ concentration would be lower and hence would give the appearance that the uptake onto the resin was higher. Nitrifying bacteria produce HNO_2 and HNO_3. Tests were carried out for NO_2^-, and NO_3^- ions. The technique used could not detect any NO_2^-, or NO_3^- ions, therefore less than 0.2% of the initial NH_4^+ ions could have been consumed biologically. The low pH caused by the presence of benzoic acid would also be too low for the growth of microbes. Therefore biological effects were ruled out.

Final NH_4^+ concentrations were measured with the ion selective electrode as explained in section 3.2.1. Tests were carried out to see if the presence of benzoic acid affected the reading obtained by the probe. Different solutions with the same NH_4^+ concentration and varying benzoic concentrations were measured. Consistent readings were obtained, even when the NH_4^+ concentration was low and the benzoic acid concentration was high.

In the upper left-hand-side of Figure 4.3 are some data predicting the maximum uptake of NH_4^+ in the presence of different organic concentrations (calculated from Langmuir isotherm equation). The experiment of "NH_4^+-only" has a maximum uptake of approximately 29mg of NH_4^+ per gram of clinoptilolite. The experiments with 10ppm, 50ppm, and 150ppm have maximum uptakes of approximately 22mg/g, 20mg/g, and 18mg/g respectively. This is most likely due to the different H^+ ion concentrations as the pH was not the same for each experiment. The pH was not the same for each

experiment as this would require the addition of more chemicals/ions; hence the effect the presence of the organic made could not be determined.

This data must be treated with caution as it is an extrapolation well beyond the data measured, hence may not be very accurate. It does however show that there is a decreasing trend in maximum uptake as the benzoic acid concentration increases. Therefore the enhancement only occurs at lower NH_4^+ concentrations. From Figure 4.3 it appears as though the organic isotherms will cross the "NH_4^+-only" isotherm at a concentration slightly higher than 90mg/l.

A similar set of experiments were carried out in which the organic pollutant used was sodium benzoate. Again there appears to be an enhancement in the presence of the organic. In the case of benzoic acid (Figure 4.3), there appeared to be a large enhancement up to 10ppm. In the case of sodium benzoate there appears to be a negligible enhancement above 10ppm. Therefore, either only a small amount of the organic is required to obtain the enhancement, or the amount of enhancement that is obtainable is limited.

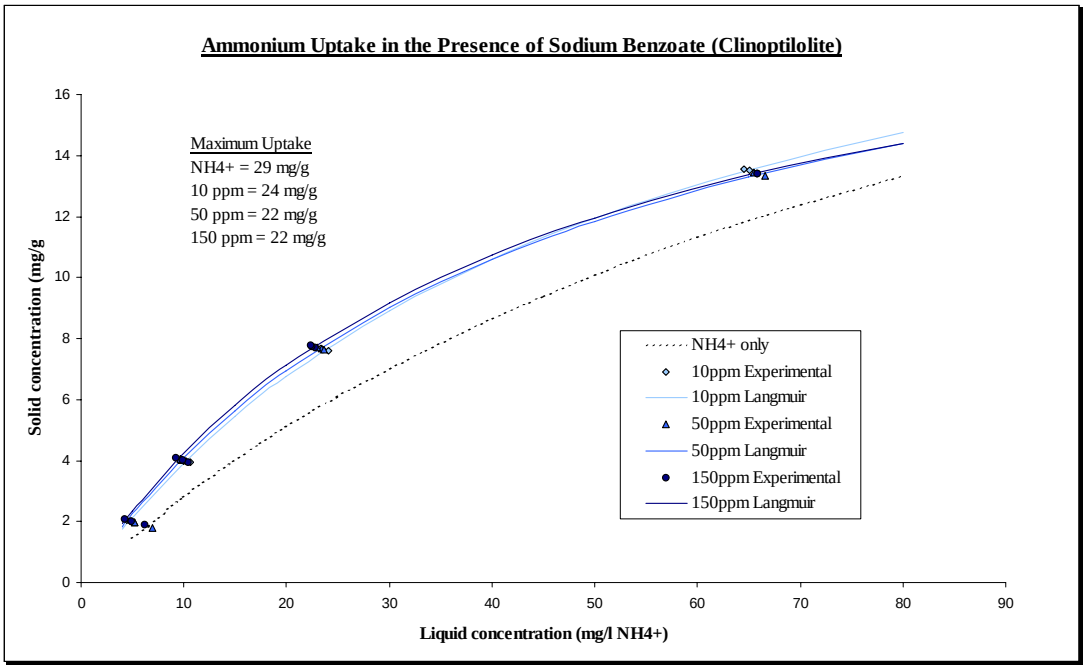


Figure 4.4: NH_4^+ equilibrium in the presence of sodium benzoate, onto clinoptilolite.

Figure 4.5 shows the equilibria in the presence of phenol. As with benzoic acid and sodium benzoate there is again an enhancement over the range of concentrations shown. Also the maximum uptake decreases as the phenol concentration increases. Phenol is a weak acid so H^+ ions may be present and may compete for ion exchange sites.

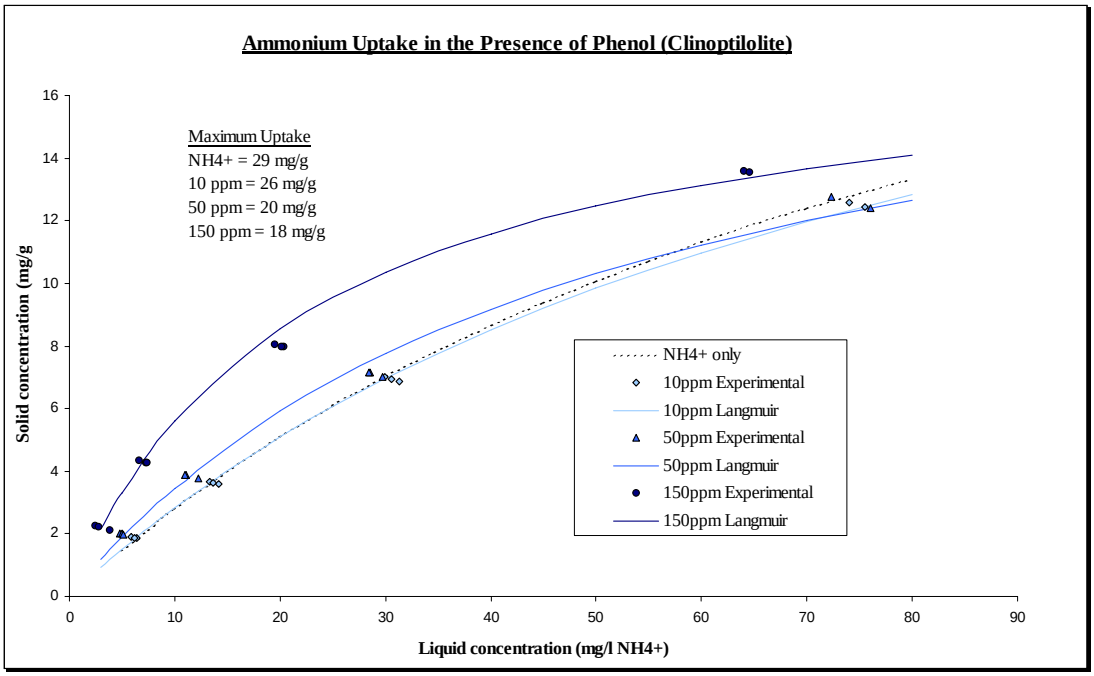


Figure 4.5: NH_4^+ equilibrium in the presence of phenol, onto clinoptilolite.

However, unlike Figures 4.3 and 4.4, there appears to be little or no enhancement at low phenol concentrations. There are a couple of possible explanations for this. Firstly, higher concentrations of phenol may be required to obtain significant enhancement. The other is that the presence of phenol may slow the rate of exchange; hence the samples may not have been not fully equilibrated. Therefore the 10ppm and 50ppm isotherms would have increased in height, thus showing an enhancement.

In the case of hexane a different procedure was adapted because of the limited solubility of hexane in water. NH_4^+ solutions were saturated with hexane, and then the excess hexane was removed. Half saturated solutions were produced by saturating NH_4^+ solutions with hexane and diluting with an equivalent amount of distilled water.

Hexane was the organic contaminant used in experiments referred to in Figure 4.6. Again the presence of the organic appeared to enhance the uptake of ammonium ions. Both concentrations of hexane appear to give similar degrees of enhancement.

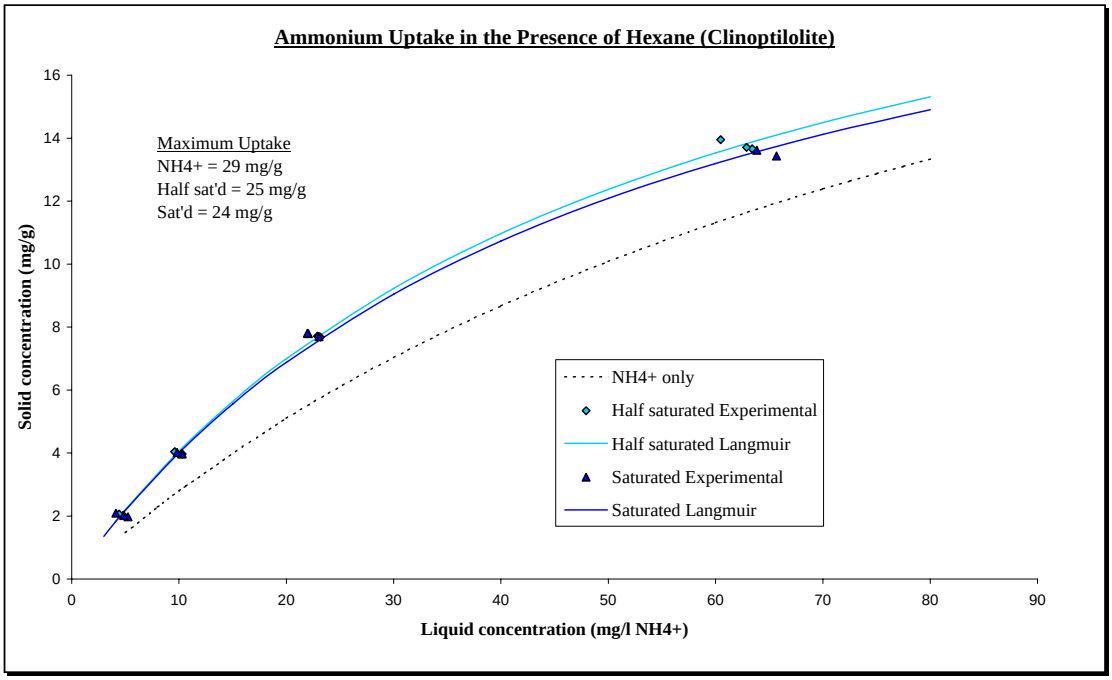


Figure 4.6: NH_4^+ equilibrium in the presence of hexane, onto clinoptilolite.

Figures 4.3 – 4.6 all show isotherms with increasing enhancement as the organic concentration increased. In figure 4.7 the isotherms of 10ppm and 50ppm lie below that of the "NH_4^+-only" curve. However there is an increasing uptake trend as the contaminant concentration rises from 10ppm - 50ppm - 150ppm.

Similar arguments to that of phenol can be used where the organic may have slowed the approach to equilibration. It is likely that the presence of glucose causes an enhancement in ion exchange because there is a trend of increased ammonium ion uptake as the glucose concentration was increased from 10ppm to 150ppm, see Figure 4.7.

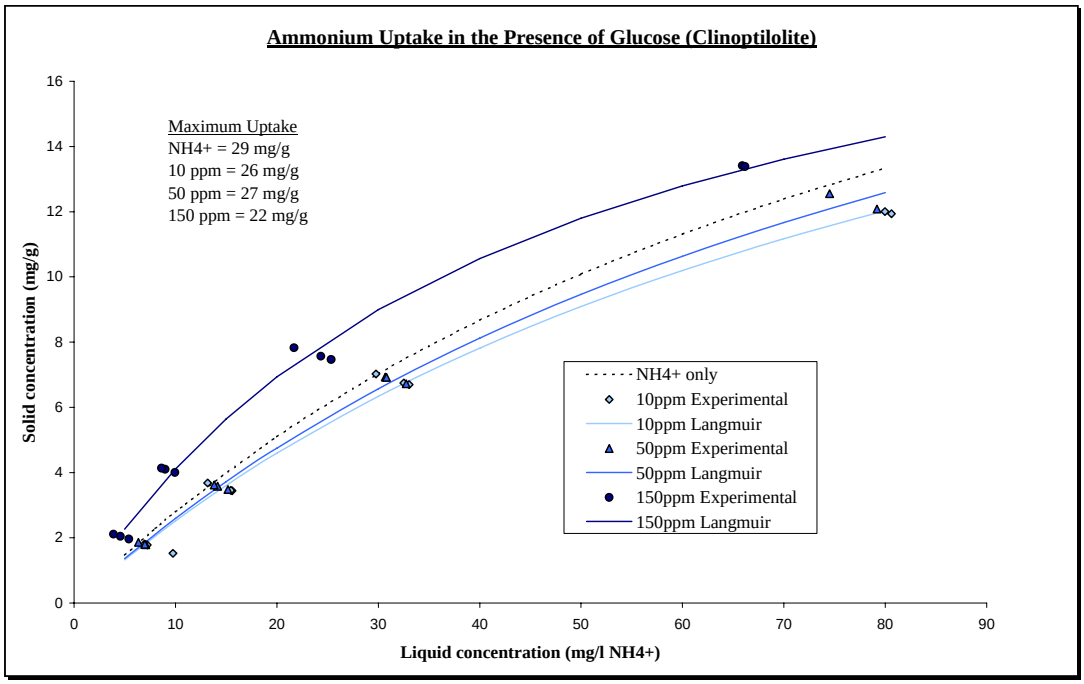


Figure 4.7: NH_4^+ equilibrium in the presence of glucose, onto clinoptilolite.

The presence of nitrifiers or other microbes was investigated and tests were carried out for nitrites and nitrates. None were detected. The solution was also tested for proteins using the Lowry Procedure and none were present. Therefore significant numbers of microbes were not present.

The presence of citric acid was studied as it is commonly used as a buffer in biological systems. It is also weakly ionic, dissociating to yield three H^+ ions. There is an unexpected enhancement of ammonium ion uptake in the presence of citric acid.

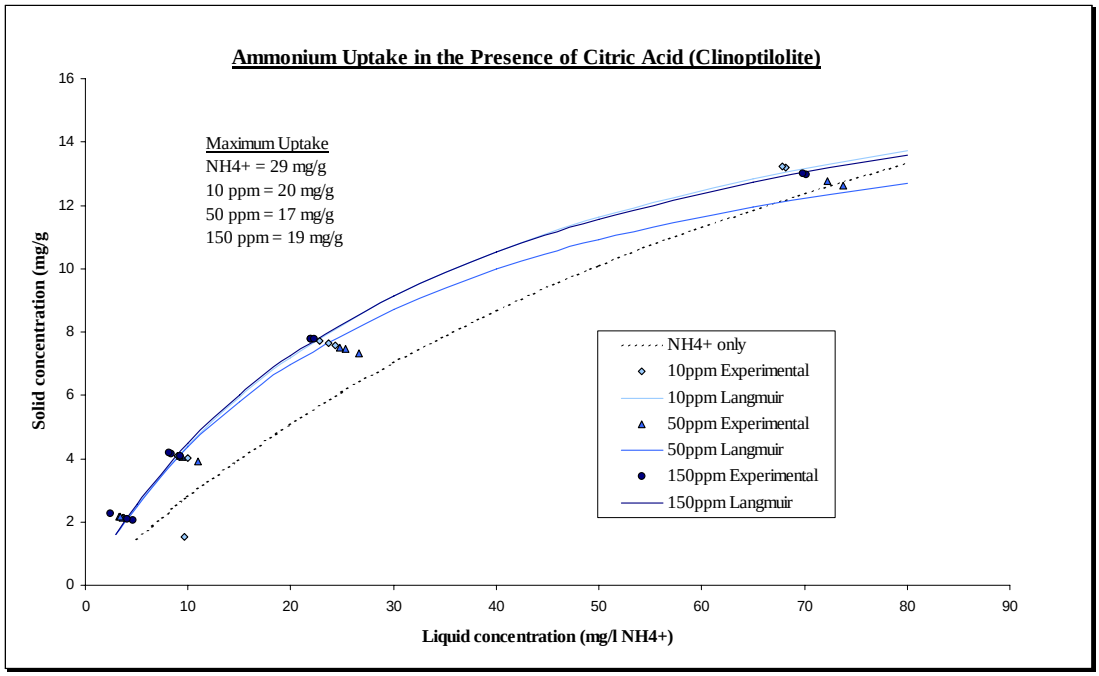


Figure 4.8: NH_4^+ equilibrium in the presence of citric acid, onto clinoptilolite.

At aqueous ammonium ion concentrations between 70mg/l and 80mg/l the isotherms in the presence of citric acid and the "NH_4^+-only" curves cross over. The predicted maximum uptakes are much lower than in the other exchangers studied in the presence of organics, see Figures 4.3 - 4.7. This can be explained by the relatively high concentration of H^+ ions which may compete with NH_4^+ ions for sites on the clinoptilolite.

Between the concentrations of 0mg/l - 70mg/l of ammonium ion in the aqueous phase there is an enhancement of NH_4^+ ions onto clinoptilolite caused by the presence of citric acid. At these low NH_4^+ concentrations the H^+ ion concentrations are relatively high. In order to obtain the enhancement observed in Figure 4.8 there would need to be a significant driving force to enhance NH_4^+ ion uptake onto clinoptilolite as the presence of H^+ ions (especially at 150ppm citric acid) will compete for the sites.

4.1.3 Equilibrium of NH_4^+ in the presence of *complex* organics, onto clinoptilolite

Figures 4.3 – 4.8 showed the equilibria of ammonium ion uptake onto clinoptilolite in the presence of some simple (low molar mass) organics. Actual wastewater can contain a complex mixture of organic pollutants including polysaccharides, lipids, proteins, and antibiotics. A selection of some representative compounds were studied and the results showing the effect of their presence upon ammonium ion uptake are shown in figures 4.9 – 4.13.

Fatty acids are often found in municipal wastewater and results for ammonium ion uptake onto clinoptilolite in the presence of stearic acid are shown in Figure 4.9. Stearic acid has a very low solubility so solutions were made as saturated and half saturated (at 20°C) in a similar manner as that for hexane solutions.

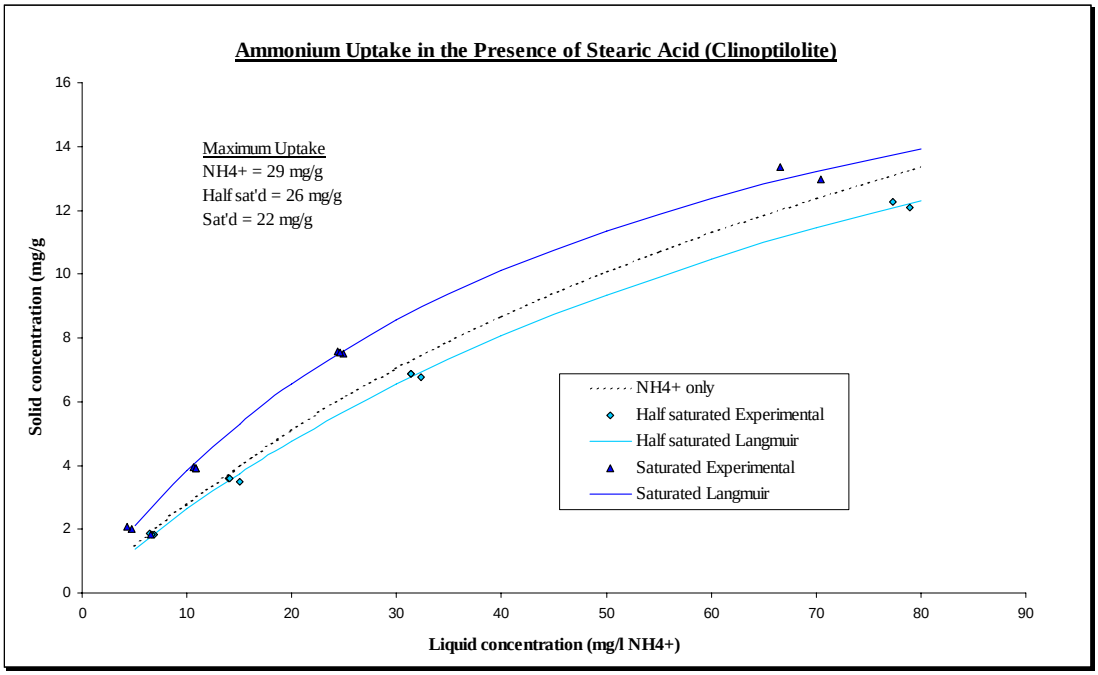


Figure 4.9: NH_4^+ equilibrium in the presence of stearic acid, onto clinoptilolite.

The isotherm for ammonium ion uptake in the presence of half saturated stearic acid solution lies beneath that for NH_4^+ alone in the water. There is evidence of increased uptake in the case of the saturated stearic acid when compared with the 50% mixture. The reason for this is believed to be similar to the reason given for glucose and phenol. The very large size of the stearic acid possibly slowed diffusion of NH_4^+ ions through the pores. Again there is a reduction in maximum uptake due to the presence of H^+ ions and fouling by the organic part of the molecule.

Proteins are another example of complex molecules found in wastewater and ion exchange equilibria results for ammonium ion uptake onto clinoptilolite in the presence of fungal lipase from candida rugosa are shown in Figure 4.10.

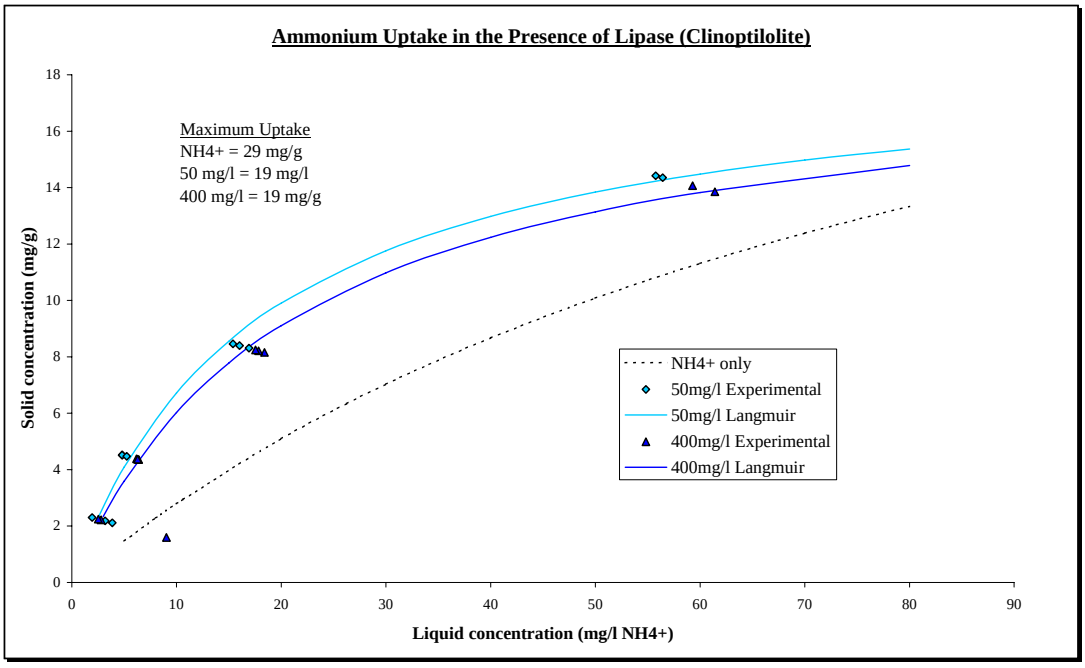


Figure 4.10: NH_4^+ equilibrium in the presence of lipase from Candida rugosa, onto clinoptilolite.

The lipase was added to the aqueous feed solution as a mixture of 30wt% lipase and 70wt% lactose. As can be seen there is a very large increase in the ammonium ion

uptake over the concentration range shown. The enhancement of ammonium ion in the presence of the lipase was larger than for any of the previous organics.

The isotherm in the presence of 400mg/l lipase lies a small amount below that at 50mg/l lipase concentration. This could be due to two possible reasons. Both may have reached a maximum enhancement and the difference is experimental error. Another possible reason is that the large size of the protein molecules lead to slow diffusion through the pores. Hence the 400mg/l experiments faced much slower diffusion and were a short distance from 100% equilibrium. Either way even a small amount of protein caused a significant enhancement of NH_4^+ ions onto clinoptilolite.

Antibiotics are occasionally added to aquaculture water to maintain a healthy fish stock [16]. The benzylpenicillin used to generate the experimental results shown in Figure 4.11 is just one of many antibiotics. It is also of interest as it contains potassium (K^+) ions, which are of particular concern as K^+ is the only *common* cation that has a higher affinity for clinoptilolite than NH_4^+ ions.

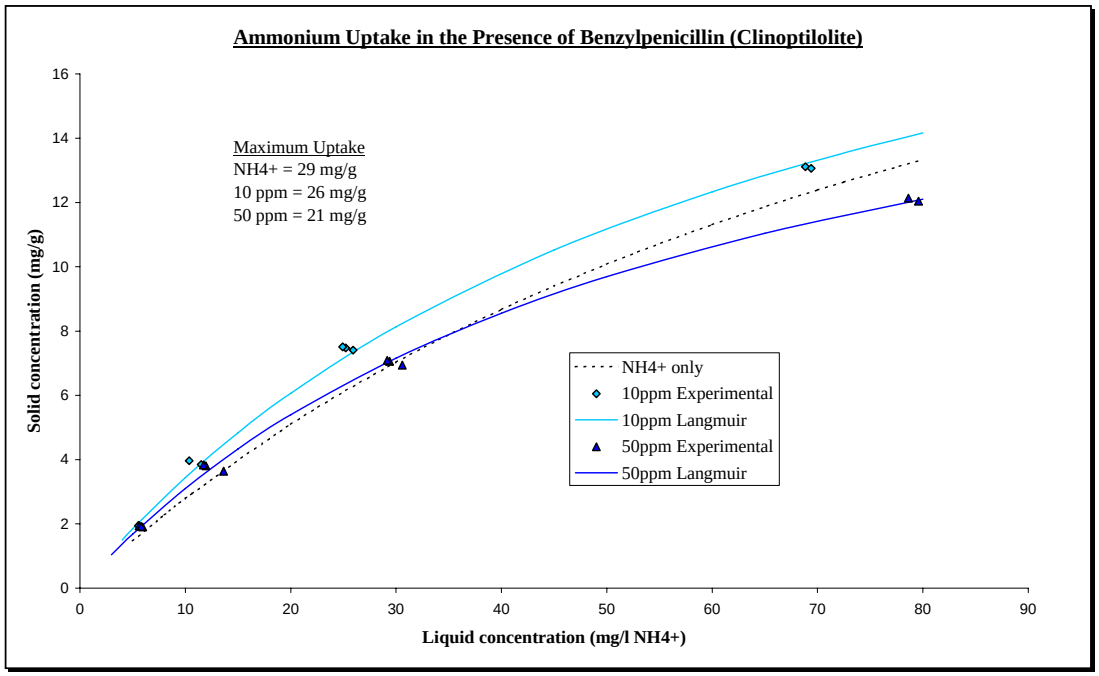


Figure 4.11: NH_4^+ equilibrium in the presence of benzylpenicillin G potassium salt, onto clinoptilolite.

The isotherm at 10ppm penicillin concentration shows enhancement of NH_4^+ ion uptake compared with the "NH_4^+-only" control. The isotherm at 10ppm shows a maximum uptake of 26mg/g, which is 3mg/g lower than that of the "NH_4^+-only" isotherm.

The isotherm at 50ppm appears to produce no enhancement at lower concentrations, and NH_4^+ uptake reduces at higher NH_4^+ concentrations to below that for the "NH_4^+-only" control. At 50ppm benzylpenicillin it is possible that the enhancement of NH_4^+ due to the presence of the organic being present is cancelled out by the competition for sites from the K^+ ion.

Sunflower oil is a common lipid (triglyceride) and was used to simulate the possible effect of lipids upon the equilibria of NH_4^+ ions onto clinoptilolite. As sunflower oil is

relatively insoluble in water, saturated and half saturated solutions were prepared at 20°C.

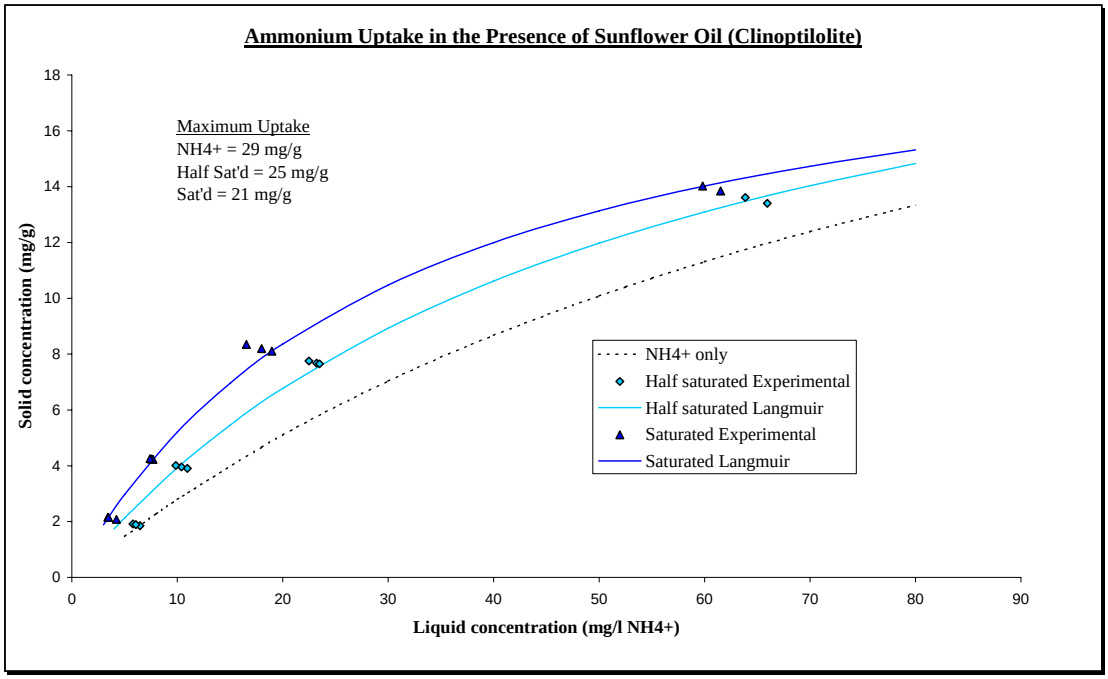


Figure 4.12: NH_4^+ equilibrium in the presence of sunflower oil, onto clinoptilolite.

There is an enhancement due to the presence of an organic and shows an increasing trend from "NH_4^+-only" to half saturated to saturated. Sunflower oil is non-ionic but as the concentration increased the predicted maximum uptake decreased from 29mg/g – 25mg/g – 21mg/g.

The free fatty acid content of the sunflower oil was very small (<1%) and therefore any chemical effects on ion exchange would be small. Any hydrolysis of the sunflower oil would also be insignificant at the temperature at which the measurements were taken.

Whey protein is a mixture of protein molecules and is a by-product of cheese making. A lipase was used earlier (Figure 4.10), but was only 30% protein, and was only one specific protein. Whey protein is a complex mixture, which is more likely to model proteins in wastewater more accurately.

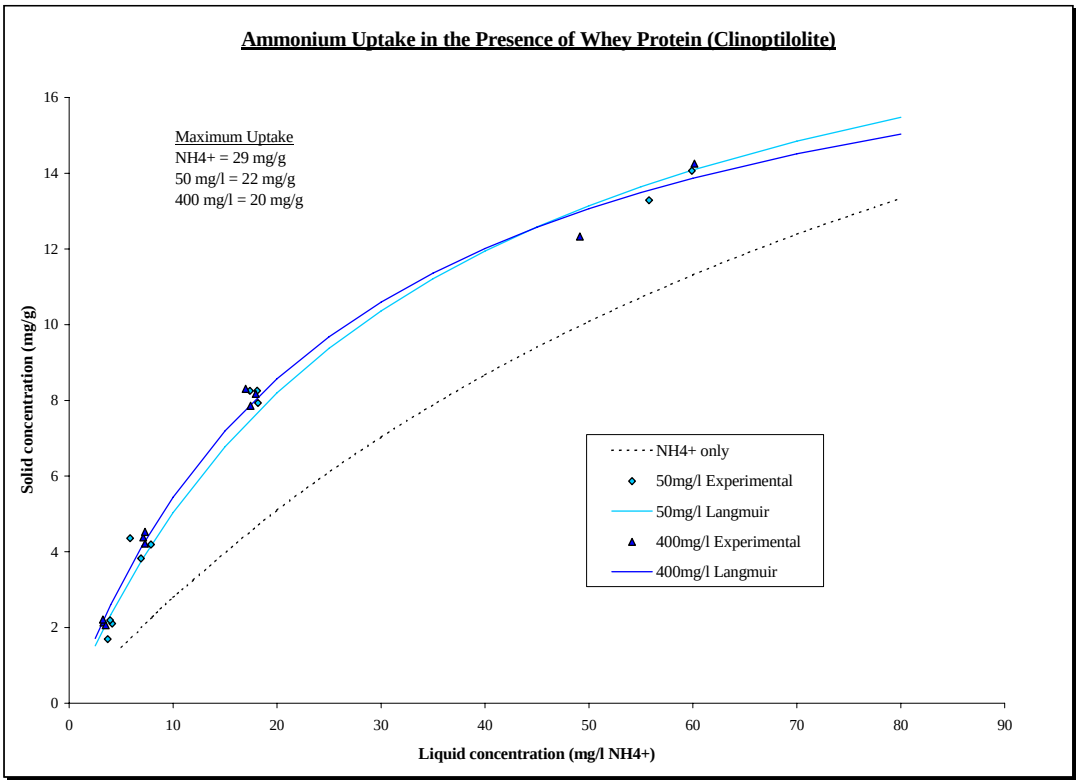


Figure 4.13: NH_4^+ equilibrium in the presence of whey protein, onto clinoptilolite.

As with the lipase (Figure 4.10) the whey protein also enhances uptake of NH_4^+ ions onto clinoptilolite. Isotherms at 50mg/l and 400mg/l whey protein concentrate show very similar amounts of enhancement. Therefore it is likely that only a small amount of protein is required to obtain significant enhancement.

The maximum ammonium uptake values decrease with increasing protein concentration, thus showing similar behaviour to that in the presence of lipase. Proteins can foul the ion exchangers. They are also weak acids, so provide H^+ ions,

which may decrease the maximum uptake. The whey protein used was about 94wt% protein, the rest was lactose with a small amount of mineral salts present.

4.1.4 General discussion of organics onto clinoptilolite

The main feature of interest in Figures 4.3 – 4.13 is the enhancement of NH_4^+ onto clinoptilolite in the presence of an organic in all cases. In some cases the presence of any concentration of organic appears to have a similar enhancement. In other cases the amount of enhancement appears to increase as the organic concentration increases. A wide range of different pollutants can be found in wastewaters, and some of these were included. Each different contaminant had different properties, simple or complex, polar or non-polar, and ionic or non-ionic. Each of these different types enhanced NH_4^+ ion uptake onto clinoptilolite.

The observed behaviour in the presence of organic compounds could be a result of a blocking effect or reversible adsorption. The isotherms were not reversed so neither of these two possibilities could be examined.

A possibility is that the presence of the organics results in small but significant changes in the structure of the zeolite, enhancing the access of ammonium ions to available fixed sites. The presence of a number of different types of fixed sites in clinoptilolite was postulated by Koyama and Takeuchi [45]. Access to these was shown to be dependent upon the composition of the external solution. Therefore the composition of the system may affect overall ion exchange capacity such as is observed here.

Another possibility is that the presence of each organic may give rise to small changes in surface tension of the aqueous phase. This may enhance access of the aqueous solution to the interior macropores of the clinoptilolite, thus allowing access to more

fixed sites. Of all the organics studied the most surface active are the proteins. The organic compounds used in Figures 4.10 and 4.13 were proteins and it was in these two cases that the largest enhancement occurred.

The results indicate the effect of certain single contaminants upon the equilibrium isotherms for ammonia uptake. Only they give no indication of the possible modification to the kinetics of uptake, which also requires detailed consideration in process and equipment design. In the case of many real effluent streams there will be a number of contaminants present simultaneously and the interacting effects of these upon ion exchange uptake would require determination in future work.

In the cases of phenol, glucose, and stearic acid there appears to be a decrease in ammonium ion capacity at the lower organic concentrations.

The "NH_4^+-only" isotherm was experimentally determined three times to confirm its precision, and to prove that it was not too low giving the false appearance of enhancement by organics.

4.2 POLYMERIC RESINS

4.2.1 Dowex 50w-x8

Clinoptilolite is a preferred ion exchanger in a number of situations compared with other zeolitic cationic exchange resins because it has a high affinity for NH_4^+ ions, and is also much cheaper than synthetic resins, although synthetic resins offer a number of different properties which may be more suitable than clinoptilolite. In this work two synthetic resins were studied, Dowex 50w-x8, and Purolite MN500.

4.2.1.1 Characterisation of Dowex 50w-x8

Figure 4.14 shows the Langmuir and Fruendlich isotherms fitted to experimental data for the uptake of NH_4^+ ions onto Dowex 50w-x8 (initially in the Na^+ form). In the case of clinoptilolite (Figure 4.1) the Langmuir isotherm was shown to be an excellent model. By comparison, the equilibrium data for Dowex 50w-x8 only show a modest fit to the Langmuir model.

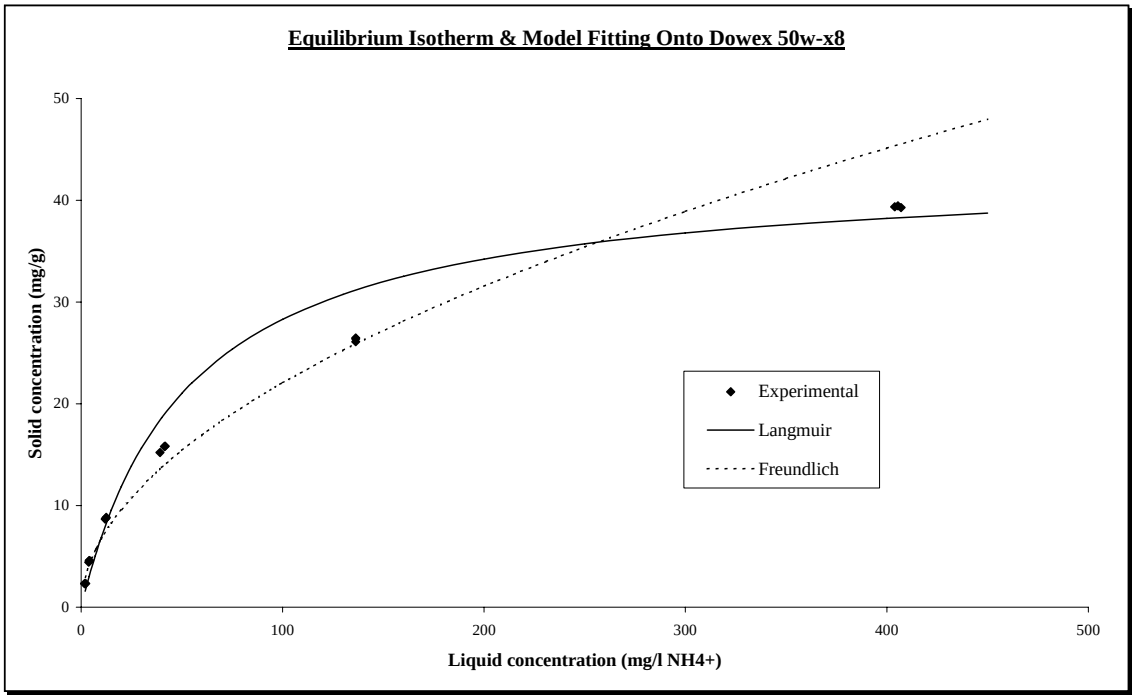


Figure 4.14: Equilibrium of NH_4^+ onto Dowex 50w-x8.

The experiments were assumed to be at equilibrium because it was found that the time required to reach equilibrium was 5 days. Each experiment was left for 7 days to be 100% sure equilibrium was obtained.

The maximum uptake for NH_4^+ onto clinoptilolite was found to be 29.4mg/g. Figure 4.14 shows that the maximum uptake of Dowex 50w-x8 is well in excess of this (possibly 2 – 2.5 times higher). The maximum uptake of NH_4^+ onto Dowex 50w-x8 was difficult to predict since neither of the adsorption models fitted the data with sufficient accuracy.

4.2.1.2 Organics onto Dowex 50w-x8

Figure 4.8 showed that NH_4^+ uptake onto clinoptilolite was enhanced in the presence of citric acid even though H^+ ions were competing for sites. Figure 4.15 shows that NH_4^+ uptake is not enhanced in the presence of citric acid onto Dowex 50w-x8.

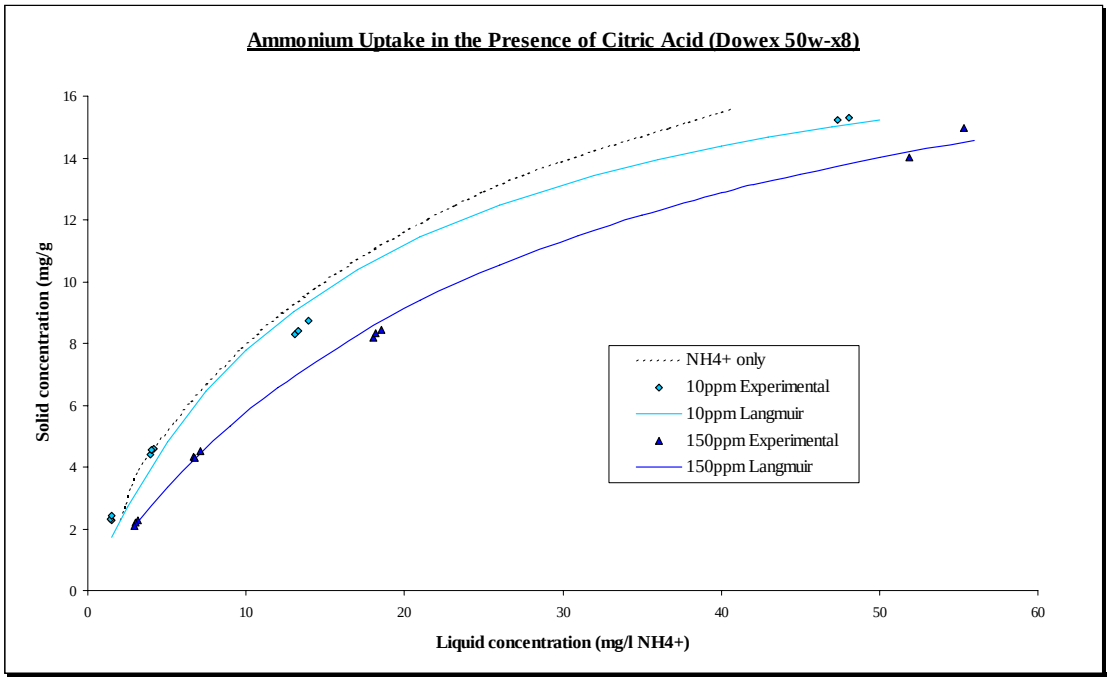


Figure 4.15: NH_4^+ equilibrium in the presence of citric acid, onto Dowex 50w-x8.

The scope for enhanced uptake in the case of Dowex 50w-x8 may be less than for clinoptilolite. It is possible that the proportion of sites available for exchange in the case of the Dowex is already close to its maximum in the absence of any organic contaminant.

The maximum uptake was not included on charts of Dowex 50w-x8 or Purolite MN500.

At low NH_4^+ concentrations (0mg/l – 25mg/l) the two isotherms in the presence of whey protein overlap the "NH_4^+-only" curve. At higher concentrations the fouling and presence of cations by the whey protein may dominate and hence there is no net enhancement occurring onto Dowex 50w-x8, unlike that of clinoptilolite in the presence of whey protein (see Figure 4.13).

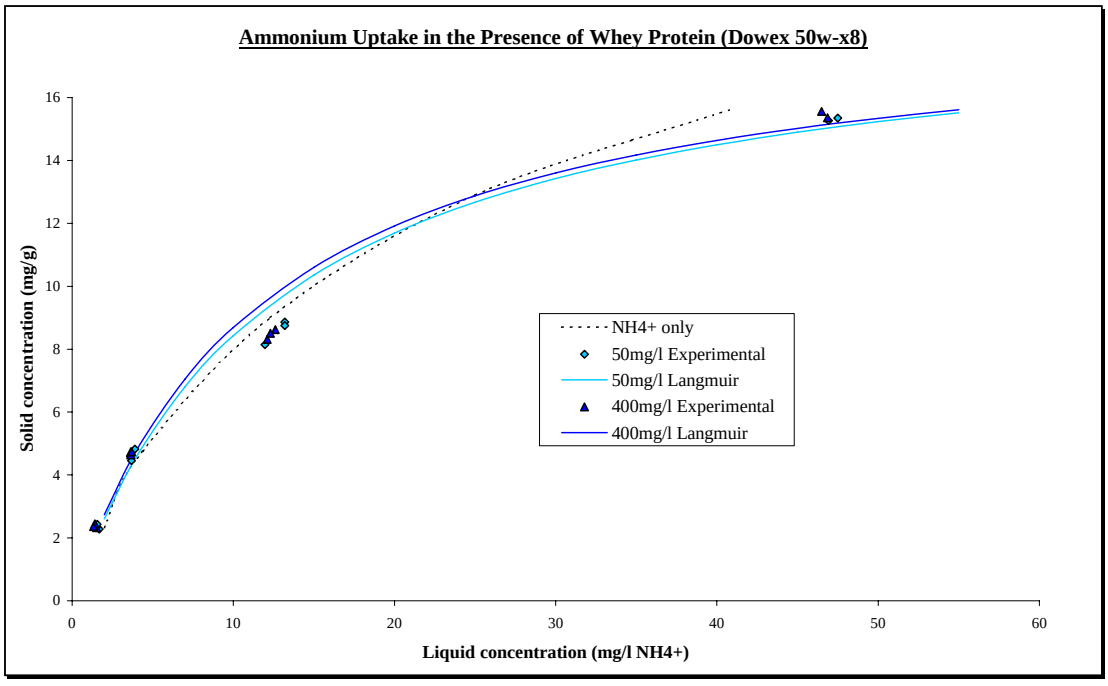


Figure 4.16: NH_4^+ equilibrium in the presence of whey protein, onto Dowex 50w-x8.

4.2.2 Purolite MN500

4.2.2.1 Characterisation of Purolite MN500

Purolite MN500 is a hyper-cross-linked macronet, cationic ion exchange resin that is reported to be resistant to fouling by organic pollutants [33]. Figure 4.15 shows the experimental data for NH_4^+ ions onto Purolite MN500 (initially in Na^+ form). Both the Langmuir and Fruendlich equations were tested for data fitting to determine if either can model NH_4^+/Na^+ on Purolite MN500.

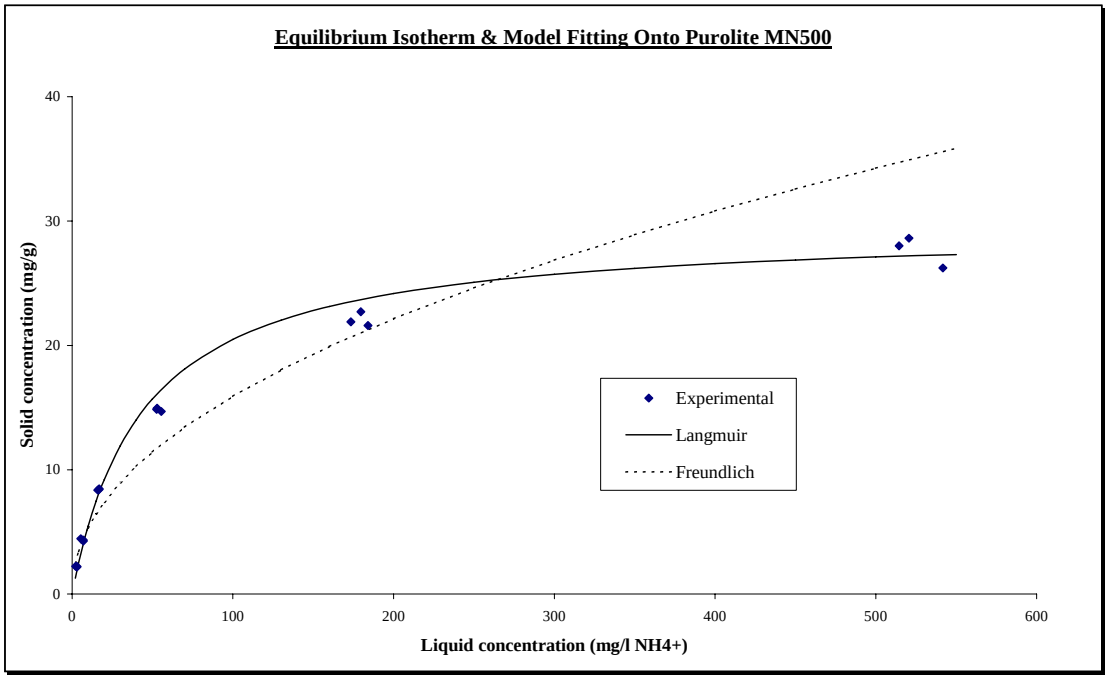


Figure 4.17: Equilibrium of NH_4^+ onto Purolite MN500.

The Langmuir model is a reasonably good fit to the experimental data. The liquid concentrations of approximately 65mg/l and 190mg/l lie beneath the Langmuir

isotherm, and the liquid concentration of approximately 530mg/l is over the Langmuir isotherm. Similar results were obtained with the ion exchange resin was Dowex 50w-x8. The Fruendlich isotherm provides a poor fit to the experimental data.

4.2.2.2 Organics onto Purolite MN500

The presence of citric acid during ammonium ion uptake onto Purolite MN500 (figure 4.18) affected uptake differently according to concentration. It is possible that uptake is enhanced due to the presence of the organic (undissociated acid), and that it is reduced due to the presence of H^+ ions. The net uptake may therefore depend upon a balance of these two effects.

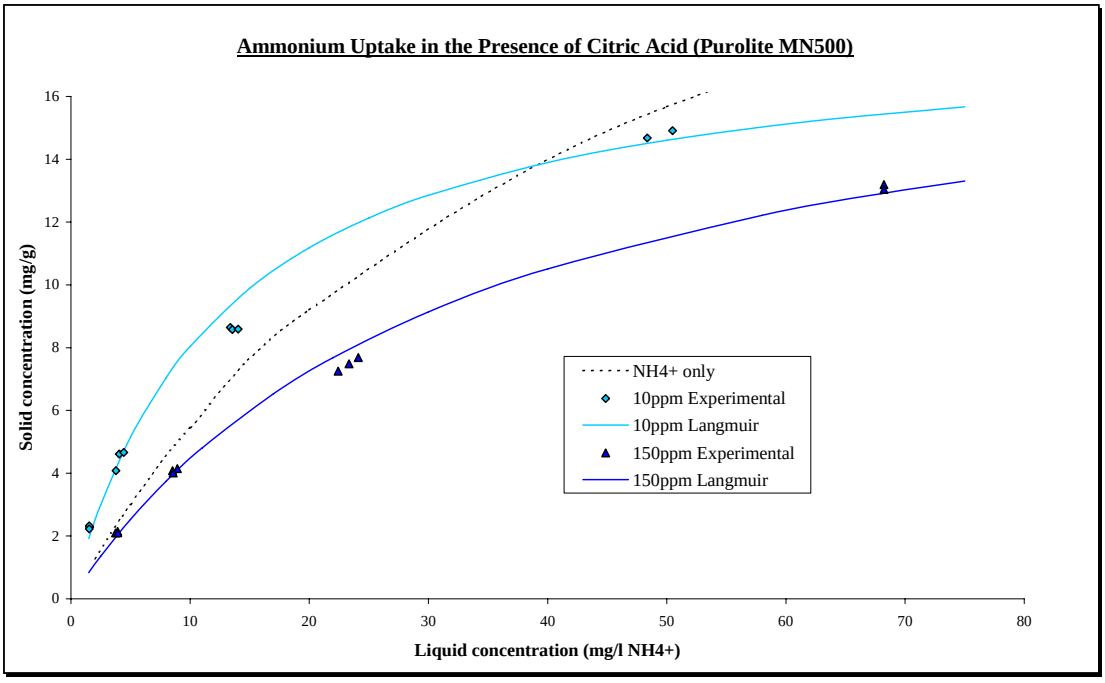


Figure 4.18: NH_4^+ equilibrium in the presence of citric acid, onto Purolite MN500.

The 10ppm isotherm shows a net enhancement from 0-40mg/l. This then drops off at higher concentrations of NH_4^+.

The 150ppm isotherm is likely to be enhanced by the presence of citric acid. Although the net effect is a lower isotherm as the competition from H^+ ions is more than the enhancement. As there are three H^+ ions per citric acid molecule the H^+ ion concentration will be close to 450ppm, many of which will be dissociated.

In Figure 4.8 equivalent data for clinoptilolite showed that the net effect was that citric acid enhanced ammonium uptake, and enhancement increased as the citric acid concentration increased. Figure 4.18 for Purolite MN500 shows that enhancement occurs, but reaches a maximum then begins to decrease. This may be a result of the "NH_4^+-only" isotherm being very high (compared with "NH_4^+-only" onto clinoptilolite), hence it is difficult for further enhancement to occur.

Figure 4.19 shows that whey protein causes an enhancement of NH_4^+ ion uptake onto Purolite MN500. The isotherms for NH_4^+ uptake in the presence of whey protein are drop below the "NH_4^+-only" isotherm (above 60mg/l NH_4^+), indicating that the whey protein may foul the resin and that in the presence of H^+ ions compete for sites.

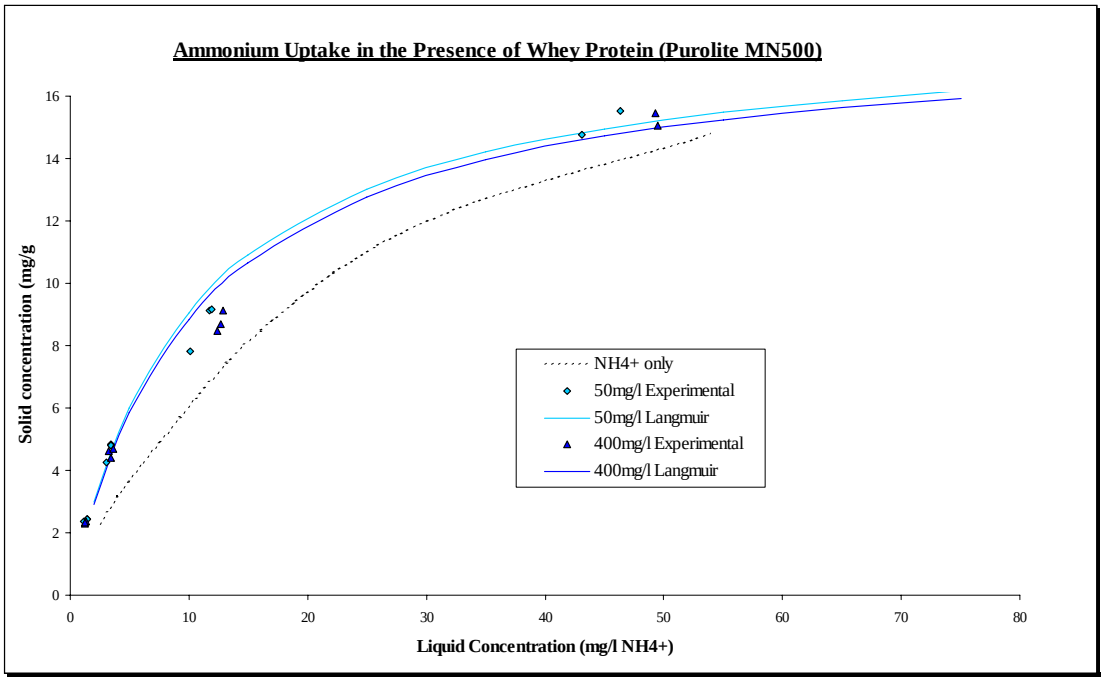


Figure 4.19: NH_4^+ equilibrium in the presence of whey protein, onto MN500.

As was seen for clinoptilolite and Dowex 50w-x8 (figures 4.13 and 4.16) isotherms the 50mg/l and 400mg/l of whey protein are very close to each other. The same effect can be seen in figure 4.19, so once again it appears as though only a small amount of protein (less than 50mg/l) is required to obtain significant uptake.

Citric acid and whey protein were the only organics experimented with Dowex 50w-x8 and Purolite MN500 because of time restrictions.

4.2.3 General discussion of organics on synthetic polymeric ion exchange resins.

Unlike, the case of clinoptilolite, where enhancement occurred each time, there was no net enhancement of ammonium ion uptake onto Dowex 50w-x8. There was a small enhancement observed in the case of Purolite MN500.

Enhancement onto Purolite MN500 is made difficult due to the NH_4^+ uptake isotherm already being high. At a liquid concentration of 30mg/l NH_4^+ the solid concentration is 7.0mg/g, 14.0mg/g, and 11.8mg/g for clinoptilolite, Dowex 50w-x8, and Purolite MN500 respectively. Dowex has the highest uptake at a liquid concentration of 30mg/l, making it difficult for any further enhancement to occur. This may explain why Dowex had no net enhancement, Purolite only a small enhancement, and clinoptilolite a significant enhancement in the presence of organics.

4.3 GENERAL DISCUSSION OF ORGANICS ONTO ALL ION EXCHANGE RESINS

Uptake of ammonium ion onto clinoptilolite was accurately modelled by the Langmuir equation. Uptake of ammonium ion onto Dowex 50w-x8 was poorly modelled by the Langmuir isotherm. Uptake of ammonium ion onto Purolite MN500 was modelled by the Langmuir isotherm much better than in the case of Dowex 50w-x8, and almost as good as in the case of clinoptilolite. Swelling of the resin is a likely explanation for this. Dowex 50w-x8 has a low degree of cross-linking; hence it swells when the larger NH_4^+ replaces Na^+ ions. As it swells pores open up and expose otherwise inaccessible sites allowing further exchange to take place at higher concentrations of NH_4^+. This is consistent with the shape of the isotherm, which does not level off in the manner predicted by the Langmuir model (see Figure 4.14). Purolite MN500 has a high degree of cross-linking, therefore swelling is minimal and the Langmuir isotherm provided a much closer fit to the experimental data. Clinoptilolite fitted the Langmuir isotherm well because the zeolite matrix is very rigid.

The presence of most organic compounds caused an enhancement of NH_4^+ uptake onto clinoptilolite and Purolite MN500. There appeared to be no net enhancement onto Dowex 50w-x8 by the presence of organic compounds. One possible explanation for

the behaviour of the clinoptilolite is that the presence of the organic compound changed the surface tension of the aqueous phase. Hence the aqueous phase may have better access to the interior macropores of the resin. This may also be a possibility in the uptakes observed in the presence of the proteins, which were the most surface active of the organics used, and which also showed the largest enhancement. A second observation, which backs up this theory, is that Dowex 50w-x8 was the only resin where no enhancement occurred, in the presence of organic species. This is also the only resin without any macropores; hence improved access would be less likely.

4.4 SORPTION OF NH_4CL

Figures 4.1, 4.14, and 4.15 showed that uptake behaviour of clinoptilolite could be modelled by the Langmuir isotherm, reasonably well for Purolite MN500, but not for Dowex 50w-x8. Experimental data for both the synthetic resins showed that they were between the Langmuir and Fruendlich models. The most likely reason for this so far has been determined to be caused by swelling of various resins.

Another possibility is that sorption of NH_4Cl was occurring. The Langmuir model predicts a levelling off to a maximum solid concentration. However this is not the case with the experimental data which showed a continuous increase of solid phase concentration with respect to solution phase concentration.

NH_4^+ sorption cannot occur otherwise a charge imbalance would occur, hence NH_4Cl sorption may be occurring. If sorption is occurring then the Cl^- ion concentration in the solution should decrease. NH_4Cl concentrations of 3.0g/l (Cl^- = 1.99g/l) were prepared and each of the three different resins was added to each sample. The experiment was carried out twice for accuracy. Table 4.1 shows that there was no loss of Cl^- ions after 6 days. Donnan invasion is another possibility and if responsible would have the same effect on the results as sorption.

Table 4.1: Chloride ion sorption test.

	Initial Cl- concentration (g/l)	Final Cl- concentration (g/l)	% of Cl- ion lost
Clinoptilolite (1)	1.99	1.98	0.3
Clinoptilolite (2)	1.99	1.97	0.9
Dowex 50w-x8 (1)	1.99	1.99	0.2
Dowex 50w-x8 (2)	1.99	1.99	0.0
Purolite MN500 (1)	1.99	1.99	0.0
Purolite MN500 (2)	1.99	1.99	0.2

To check if NaCl had sorbed onto the resin during preconditioning another test was carried out to see if Cl^- ions would leach out of each of the three exchangers into distilled water. After 6 days no chloride ions were detected. All three resins were initially preconditioned with NaCl so there is the possibility that NaCl sorption occurred. Therefore when the 3.0g/l NH_4Cl was ion exchanged some of the NH_4Cl displaced the NaCl and sorbed onto the resin. Although if NaCl sorption did occur during preconditioning it would be expected that it would leach off into distilled water.

Table 4.2: Chloride ion leachate test.

	Initial Cl- concentration (g/l)	Final Cl- concentration (g/l)
Clinoptilolite	0.0	0.0
Dowex 50w-x8	0.0	0.0
Purolite MN500	0.0	0.0

Tables 4.1 & 4.2 show that no NH_4Cl sorption occurred, nor was there any sorption to begin with otherwise it would have leached off.

Donnan invasion was not responsible because for the poor fit (especially Dowex) of the experimental data to the Langmuir model. If it were responsible the Cl^- concentration would have decreased. Table 4.1 shows that this did not occur.

4.5 COMPARISON OF CATIONIC RESINS

Figure 4.20 is a combination of figures 4.1, 4.14, and 4.17. It shows that Dowex 50w-x8 has the highest capacity, followed by Purolite MN500, and then clinoptilolite. (NB. The lines fitted through the experimental points are smooth curves and not models of any kind). Clinoptilolite has the smallest capacity but is much cheaper than the synthetic resins.

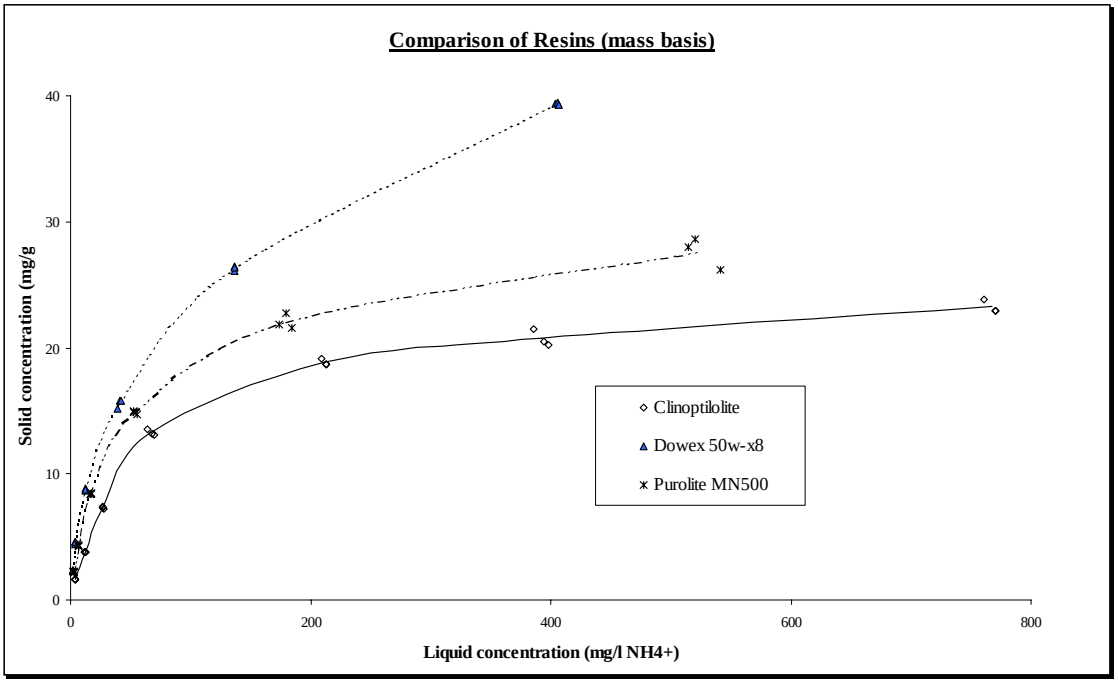


Figure 4.20: NH_4^+ equilibrium for each ion exchange resin (mass basis).

4.6 SELECTIVITY

Figure 4.21 shows the selectivity of NH_4^+ ions onto clinoptilolite and Purolite MN500, which were initially in the Na^+ form. Values were calculated from the Langmuir isotherms in Figures 4.3 and 4.17, and experimental data. Data for Dowex 50w-x8 were not included, as they did not fit the Langmuir isotherm.

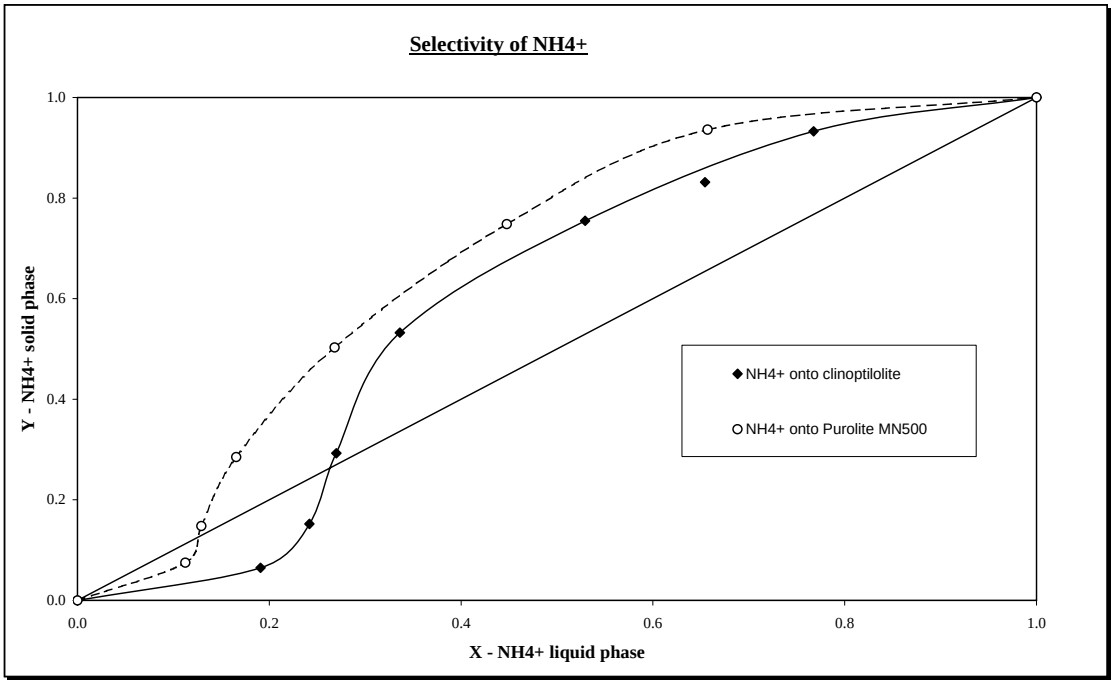


Figure 4.21: Selectivity of clinoptilolite and Purolite MN500.

Figure 4.21 is different from the isotherms where the solid and solution phases are plotted against each other. The y-axis (Y) is the solid phase mole fraction, and the x-axis (X) is the solution phase mole fraction of NH_4^+ in the binary mixture of NH_4^+ and Na^+.

Selectivity:

- Clinoptilolite = 2.7
- Purolite MN500 = 4.3

Purolite MN500 has a higher selectivity for NH_4^+ over Na^+ than clinoptilolite does. Clinoptilolite is well known to have a high selectivity for NH_4^+ yet Purolite is even higher (relative to Na^+).

The importance of this observation is in the context of treatment systems in which varying degrees of salinity occur and where Na^+ is usually the most common cation. The presence of competing ions lowers the apparent capacity of a packed bed to remove NH_4^+. Due to Purolite MN500 having a higher selectivity than clinoptilolite for NH_4^+ over Na^+ it is able to negate the capacity loss more effectively. The selectivity for other common cations K^+, Ca^{2+}, and Mg^{2+} is not known.

A higher selectivity for NH_4^+ makes regeneration easier as there will be fewer K^+, Mg^{2+}, and Ca^{2+} ions, which are much slower to be removed.

4.7 TERTIARY TREATMENT OF WOOL SCOUR WATER RESULTS

It was initially expected that the uptake of NH_4^+ from woolscour water would be slightly less compared to pure solutions of ammonium ion due to fouling and competitive uptake from other cations. This holds true for concentrations of ammonium ion below 200mg/l. However at higher concentrations uptake onto clinoptilolite is significantly enhanced and exceeds the maximum capacity of the "NH_4^+-only" isotherm, see Figure 4.22.

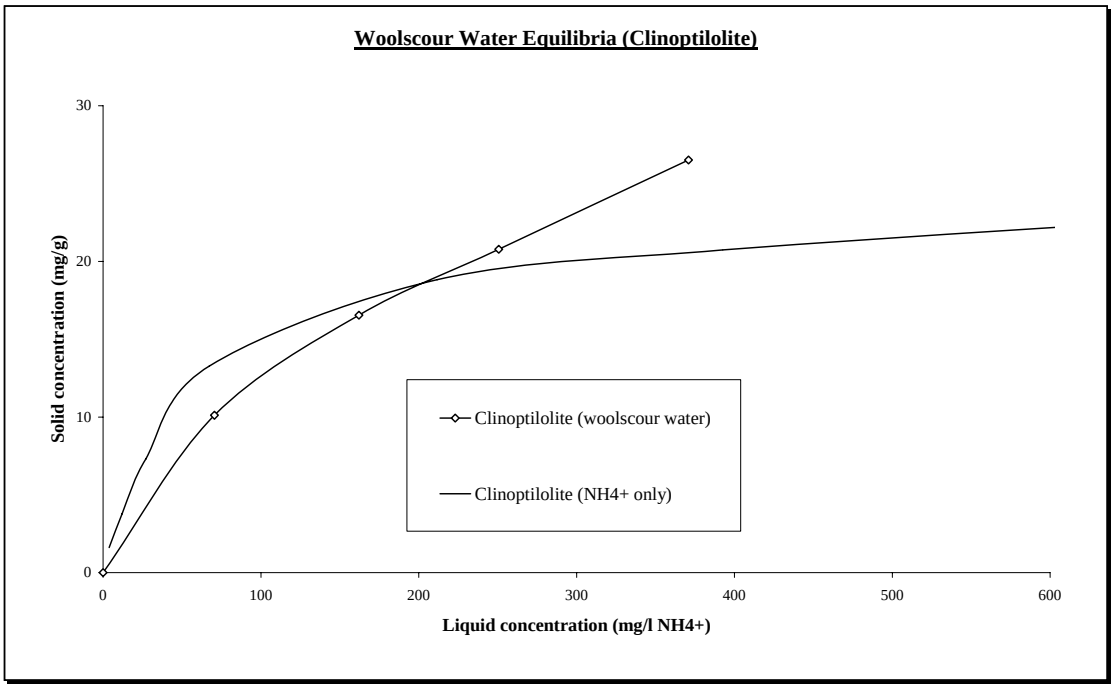


Figure 4.22: NH_4^+ equilibrium of woolscour water onto clinoptilolite.

The results for uptake onto Dowex 50w-x8 shown in Figure 4.23, are surprising in that the shape of the curve is tending upwards, suggesting that uptake is enhanced at higher solution phase concentrations of ammonium ion.

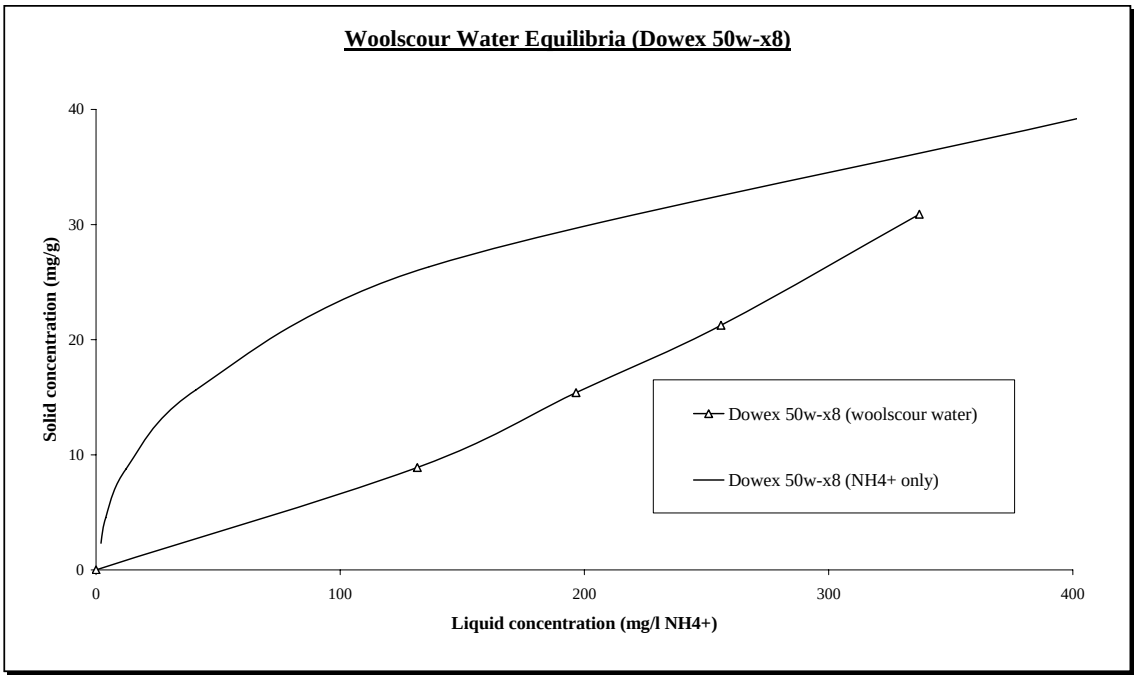


Figure 4.23: NH_4^+ equilibrium of woolscour water onto Dowex 50w-x8.

The results obtained for NH_4^+ uptake onto Purolite MN500 (Figure 4.24) are also surprising in that the isotherm is almost linear.

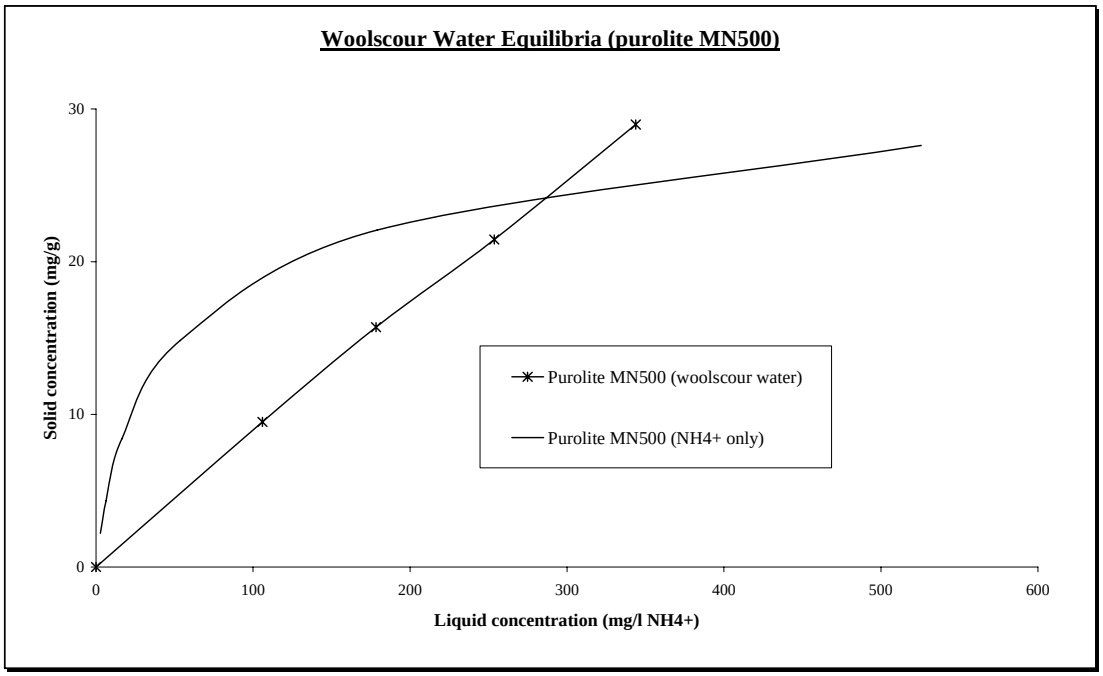


Figure 4.24: NH_4^+ equilibrium of woolscour water onto Purolite MN500.

Reasons for the results obtained in Figures 4.22 – 4.24 are not understood. Analytical error is considered unlikely as the probe is highly selective towards NH_3 molecules and the repeatability was also checked.

5.0 ADSORPTION, RESULTS & DISCUSSION

5.1 ADSORPTION OF AROMATICS AND PROTEINS

In the previous chapter organics were added to determine the effect their presence may have on NH_4^+ equilibria. In this chapter the adsorptive uptake of proteins and aromatic compounds onto the ion exchangers is examined.

Figure 5.1 shows the results of adsorption of phenol onto five different adsorbents. The five adsorbents used were the three ion exchangers and two neutral adsorbents, Advanced Filtration Media and activated carbon. The experiments were carried out at three different pH values, 3.0, 11.0 and one with no pH adjustment.

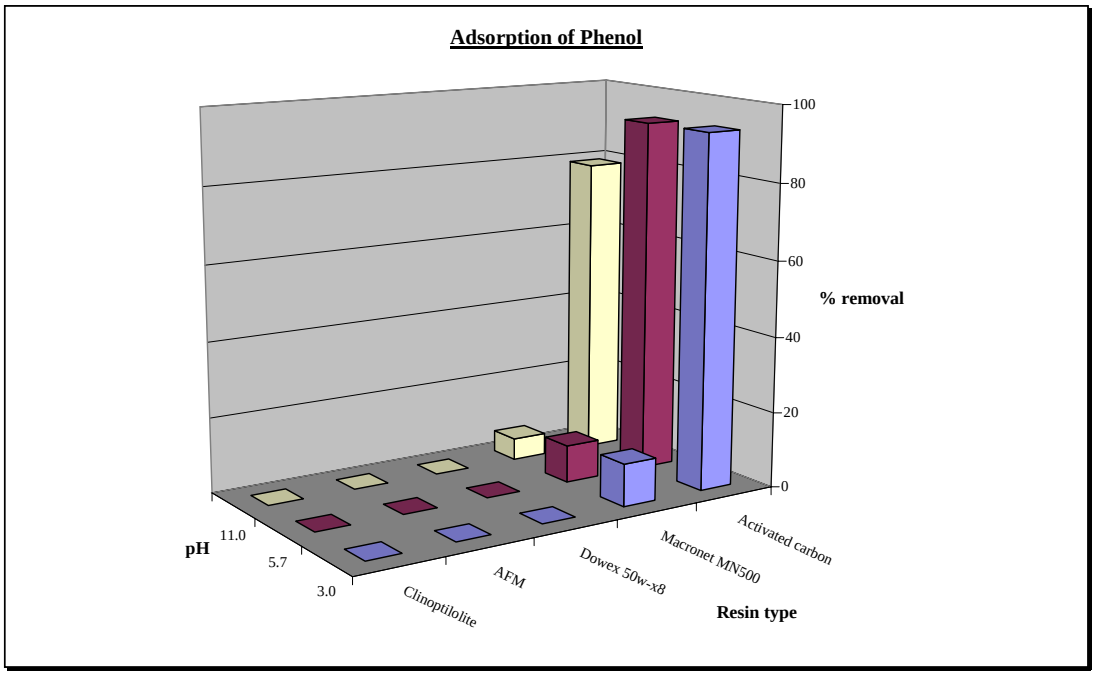


Figure 5.1: Adsorption of phenol. (Initial conc = 2.5mmol/l).

It is well known that activated carbon works well for both gas and liquid phase adsorption of organic species [9]. Zeolites are also well known to work well as gas phase adsorbents, such as molecular sieves for drying or organic adsorption [13,14]. No literature could be found on adsorption of organics onto clinoptilolite in the liquid phase except for lipase from Candida rugosa [19]. It was believed that if clinoptilolite were a very good gas phase adsorbent then it would also be very good in the liquid phase. But as can be seen from Figure 5.1 no adsorption was observed across a range of pH values.

The macronet MN500 from Purolite exhibited a small amount of adsorptive capacity for phenol, but this was much lower than that of activated carbon. It can be seen that with both the Purolite MN500 and the activated carbon the adsorption is slightly lower for the phenolate ion (i.e. pH = 11.0). The ability of MN500 to work as an adsorbent for phenol is likely to be insignificant.

The adsorption of benzoic acid showed results (Figure 5.2) that were very similar to those for phenol, which is not surprising since both molecules are similar. There are two points of interest though. The first is that the adsorption of benzoic acid onto MN500 was higher than that found by phenol, as both phenol and benzoic acid had the same molar concentration. The second is that the adsorption of the benzoate ion (pH = 11.0) is poor compared to that observed at lower pH, see Figure 5.2.

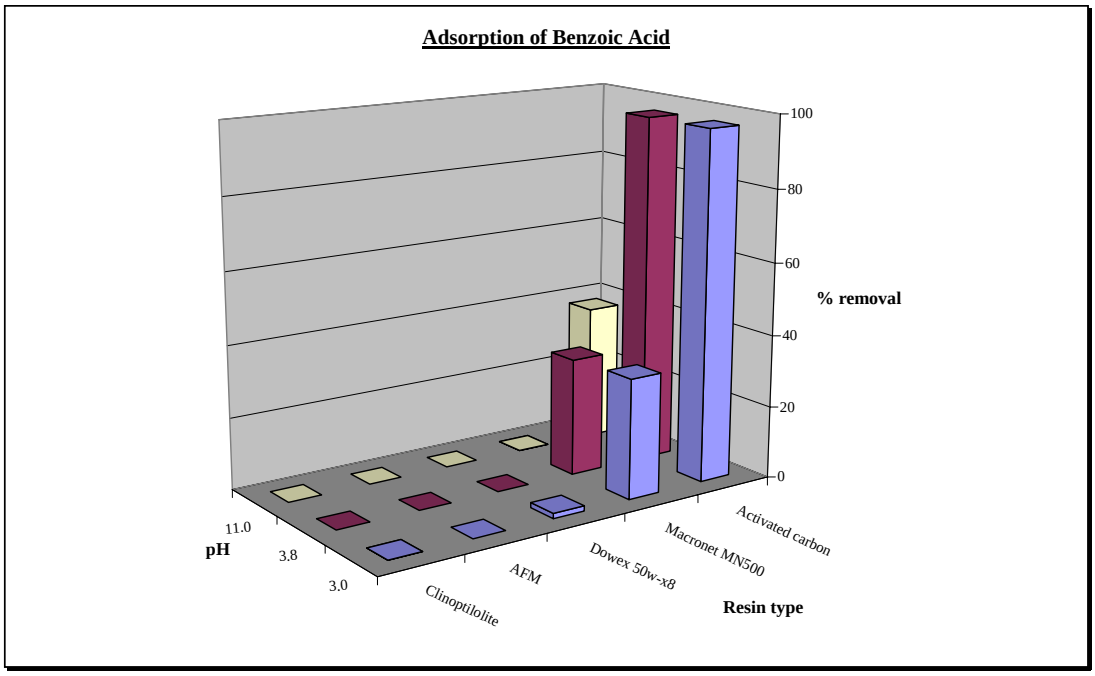


Figure 5.2: Adsorption of benzoic acid. (initial conc = 2.5mmol/l).

The adsorption behaviour of whey protein appears to be complex, see Figure 5.3. Activated carbon and Purolite MN500 show the highest removal. In the cases of phenol and benzoic acid uptake activated carbon was a much better adsorbent. For whey protein the adsorption behaviour of activated carbon and Purolite MN500 are comparable. The other three ion exchangers also show some adsorptive capacity compared with Purolite MN500.

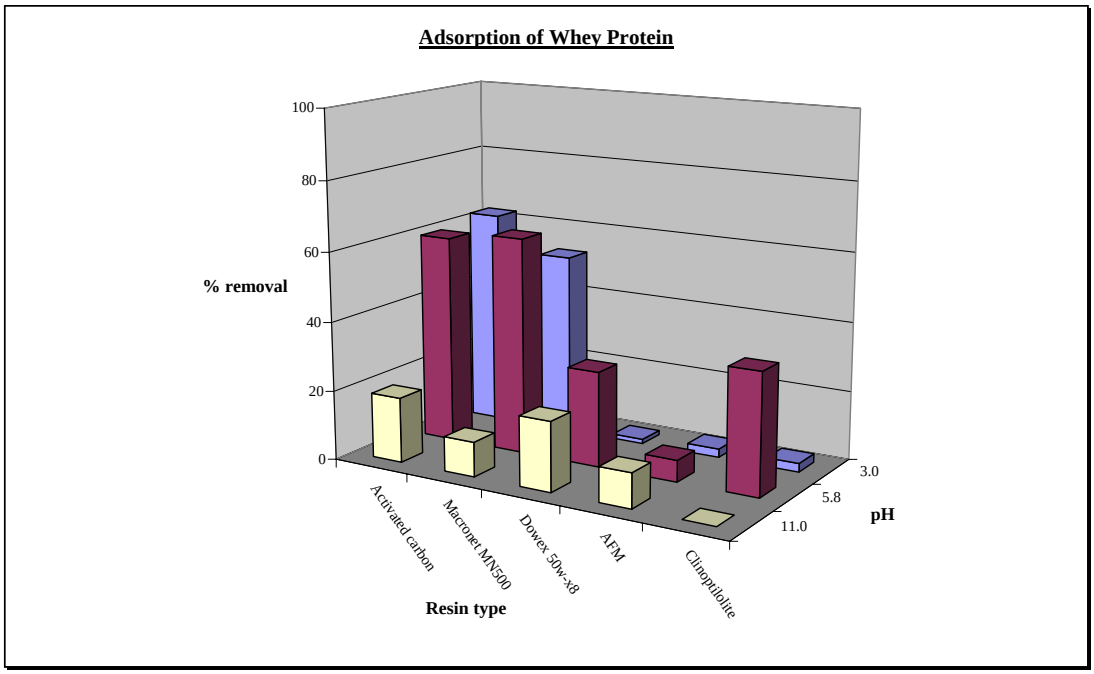


Figure 5.3: Adsorption of whey protein. (Initial conc = 0.4g/l).

A possible reason for the behaviour is that whey protein is a mixture of proteins. It is possible that different proteins were adsorbed onto different resins, and at different pH values as each protein has a different isoelectric point. The analytical test (Lowry procedure) only tests for total concentration of proteins, not specific ones.

The three ion exchange resins could be taking up proteins by ion exchange and/or adsorption, and thus may explain why MN500 has a comparable capacity for whey protein isolate to activated carbon. This may also explain why AFM has the lowest uptake as it neither adsorbs or ion exchanges.

5.2 GENERAL DISCUSSION OF ADSORPTION

The results from this chapter show that activated carbon performed much better and consistently than any other adsorbent. Only three organic compounds were covered in

this section and there is scope to extend this work to other organic compounds in the future.

Only three organics were studied others may adsorb onto clinoptilolite or Dowex 50w-x8. Wastewaters contain a complex mixture of contaminants including polar, non-polar, ionic, non-ionic, and sparingly soluble contaminants.

If organics could be adsorbed onto the ion exchange resins at the same time that the resin is removing NH_4^+ ions, then two separate operations could be combined into one. It appears as though none of the three ion exchange resins would be suitable as an adsorbent. Purolite MN500 did show some adsorptive capacity but on the basis of the compounds studied here this is unlikely to be of commercial significance. Even if the ion exchange resins could selectively remove some organic compounds, another method such as activated carbon would still be required for total removal.

6.0 COLUMN STUDIES, RESULTS & DISCUSSION

The results of the fixed bed ion exchange studies are presented. Table 6.1 summarises the range of feed compositions which were feed to each of the columns containing clinoptilolite, Dowex 50w-x8, and Purolite MN500.

Table 6.1: Pollutant concentrations.

COMPOUND	**CONCENTRATION**
NH_4^+	50mg/l (50ppm), (148mg/l NH_4Cl)
Citric acid	50ppm (0.533g/l)
Glucose	50ppm (0.50g/l)
Phenol	50ppm (0.261g/l)
Hexane/sunflower oil	Saturation
Whey protein isolate (WPI)	20mg/l
Na^+	100ppm (0.324g/l NaCl)

6.1 CLINOPTILOLITE BREAKTHROUGH CURVES

Figure 6.1 shows the breakthrough characteristics for ammonium uptake onto clinoptilolite in the presence of each organic contaminant. It can be seen that breakthrough for the "NH_4^+-only" column occurs at approximately 270 bed volumes (breakthrough ~ $0.04(C_o/C_I)$). The column with NH_4^+/citric acid broke through after about 230 bed volumes and NH_4^+/(glucose, phenol, whey protein, and hexane/sunflower oil) broke through after approximately 290 bed volumes. In the presence of organics very little difference is observed in breakthrough.

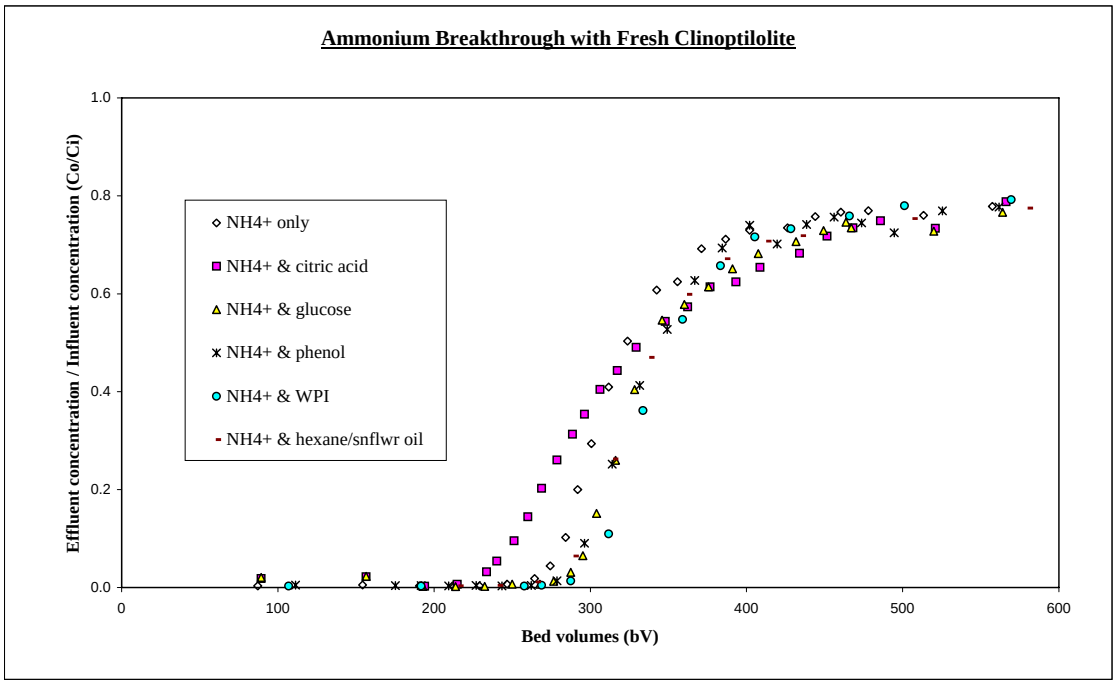


Figure 6.1: Ammonium ion breakthrough in a column of fresh clinoptilolite.

The slight reduction in the presence of citric acid can perhaps be attributed to the H^+ ions competing for sites. Another observation that can be seen is that the breakthrough zone in the presence of citric acid is wider than the other two.

There is a slight increase in the bed capacity in the presence of glucose, which is consistent with the isotherm data shown in Figures 4.3 – 4.17. The extension in bed life is less than 10%. This is very different to the batch isotherms where the presence of the organic caused much larger enhancement of NH_4^+ ion uptake.

When phenol was present the breakthrough was very similar to that of glucose. Figure 5.1 showed that clinoptilolite did not take up any phenol by adsorption. This was also confirmed during the column run, as the smell of phenol was noted in the column outlet immediately after the column was started. Experiments conducted in the presence of whey protein, hexane, and sunflower oil all showed similar results to those including glucose and phenol.

One of the most surprising observations in Figure 6.1 is that the outlet concentration levels off at approximately 0.8 (or 80% exhaustion). Therefore 20% of the inlet NH_4^+ is still being removed. There are a number of possible explanations for this phenomenon.

There are 4 different sites present within a clinoptilolite crystal (M1, M2, M3, and M4) as described in chapter 1.0. One possibility is that one of these sites is associated with slow exchange of ions.

Another possibility is slow diffusion of ions to and from a few of the ionic sites within the particle. During the preparation of the clinoptilolite the particles were ground and classified. It is possible that during grinding some of the pores collapsed, as has previously been observed in activated carbon [16], hence slowing diffusion.

The 10mg/l ammonia removal observed after breakthrough was unlikely to be caused by nitrifiers. The outlet was regularly tested for nitrites and nitrates and none were detected. A simple nitrogen balance would indicate that if nitrification was occurring the sum total of NO_3^- + NO_2^- should be 10ppm. In the case of nitrifiers, very little of the NH_4^+ is used in cell growth. The test used for nitrites/nitrates could determine levels below 1ppm. Hence nitrification was not responsible for the removal of 10mg/l. There were no signs of other microbial growth such as dissolved oxygen drops.

After 580 bed volumes had been treated, samples were taken from each of the sample ports in the column. The results are shown in Figure 6.2. The results show that there is no distinct second breakthrough curve moving through the bed. In both cases the data are almost linear showing that each part of the bed is still removing some NH_4^+. There is a slight curvature in the data points; this can be attributed to the initial regions of the bed being exposed to NH_4^+ for longer periods.

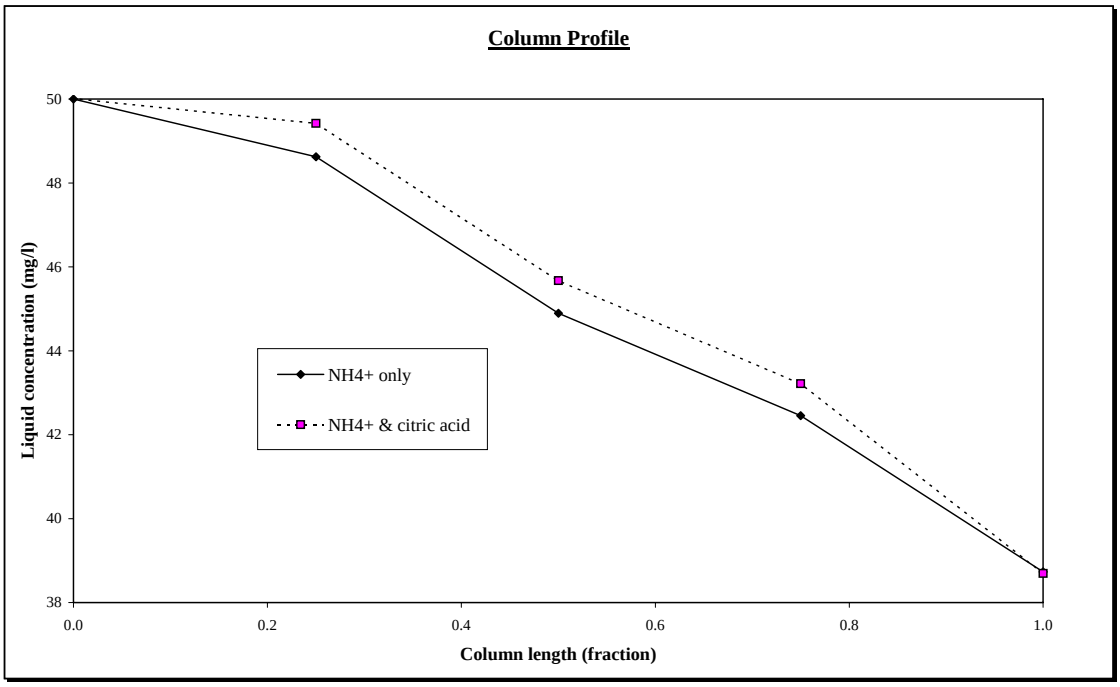


Figure 6.2: Column profile of exhausted resin.

Figure 6.3 shows the breakthrough curve for "NH_4^+-only" solutions passing through a column of clinoptilolite. Unlike the experimental data in Figure 6.1 where fresh exchanger was used each time, Figure 6.3 presents data in which the same resin was used and regenerated between each run.

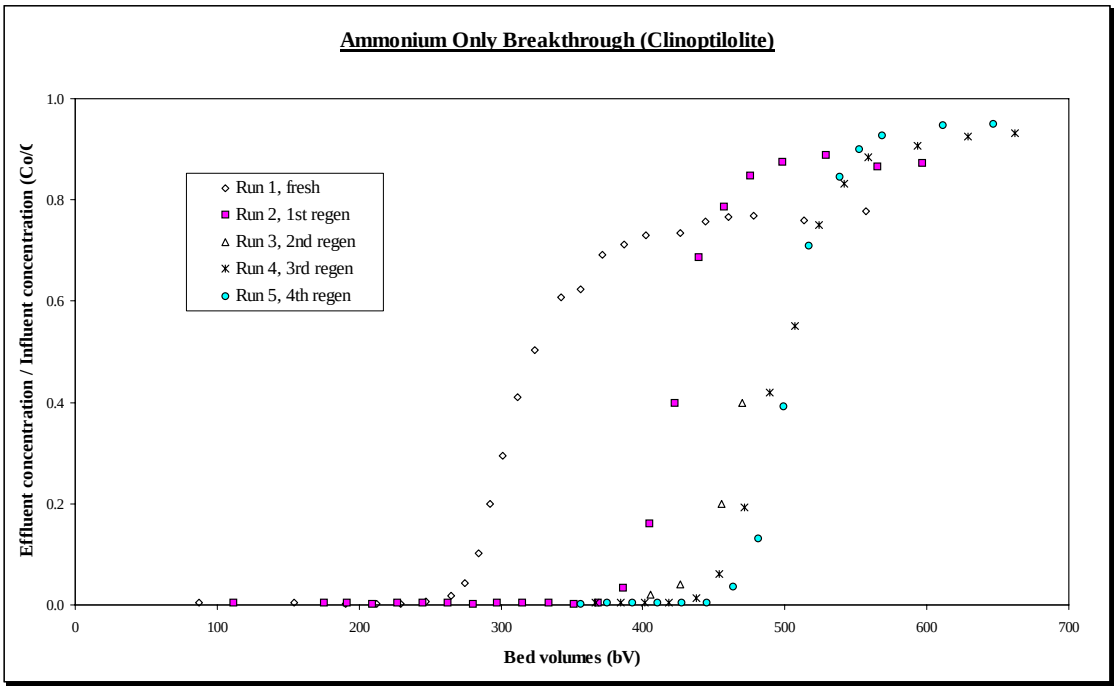


Figure 6.3: Ammonium ion breakthrough in a column of clinoptilolite.

N.B. Run 3 was stopped shortly after breakthrough due to equipment failure. This did not affect the results of the data shown or any other experimental run contained within this report.

There are two very important observations to take out of Figure 6.3. The first is that after each run the end of the breakthrough curve gets closer to 1.0, i.e. less influent NH_4^+ is being removed after breakthrough has occurred, after a few runs.

One possible explanation for the breakthrough curve approaching 1.0 after each run may be explained by the slow kinetics of the few sites responsible for NH_4^+ removal after breakthrough. These sites, which have difficult access, appear to have slow kinetics in exchanging NH_4^+ for Na^+ ions. The same could also hold true during regeneration when Na^+ ions are exchanged for NH_4^+, especially as regeneration occurs over a very short time frame. The result of this is that the ionic sites associated with

slow diffusion within the resin will be saturated with NH_4^+. Therefore these sites can no longer take part in ion exchange.

The second observation is the increase in volume treated until breakthrough occurs. There appears to be significant increases in capacity for each run and breakthrough reaches a maximum at approximately 460 bV.

One possibility is that during each cycle of uptake and regeneration the structure of the clinoptilolite was modified causing more sites to become exposed. If the structure was modified it may also explain why the removal capacity after breakthrough disappears. Sites that initially exhibited slow kinetics may have become more exposed. Hence more sites took part in ion exchange before breakthrough rather than after it.

The most likely explanation is that the clinoptilolite was not in a homoionic form (Na^+) to start with, despite being preconditioned. A previous study [14] found that pre-treatment with Na^+ removed all ions except Mg^{2+}. However concentrated solutions of NH_4^+ ions at 80°C could remove Mg^{2+} ions. The clinoptilolite then could be returned to a homoionic form (Na^+) form by alkaline regeneration. This does fit with the observed behaviour as the natural untreated clinoptilolite would have contained reasonable amount of K^+, Mg^{2+}, and Ca^{2+}, the preconditioning would not have removed Mg^{2+}.

Therefore as the service cycle proceeds NH_4^+ ions are displacing Na^+ and Mg^{2+} ions. Breakthrough occurs when all of the Na^+ has been displaced with NH_4^+. The displacement of Mg^{2+} is very slow hence it can initially only remove approximately 10mg/l. Na^+ then displaces NH_4^+ from all sites including those that initially contained Mg^{2+}. The service cycle then proceeds again with more sites in the Na^+ form. A larger volume is treated until breakthrough and less Mg^{2+} is present to remove NH_4^+ after breakthrough.

Equation 1.6 shows a selectivity order for clinoptilolite. However within each clinoptilolite crystal are 4 different sites (M1, M2, M3, and M4), each with its own selectivity order. Site M4 has a very strong selectivity for the Mg^{2+} ion and it is possible that this is where this phenomenon is occurring. Whilst NH_4^+ can displace Mg^{2+} from the M4 site if Mg^{2+} is present in the influent solution being treated there will be a large loss in capacity. This is because the M4 site will not participate in ion exchange due to its very high selectivity for Mg^{2+}.

The reason behind the two significant findings (increase of breakthrough, and 10mg/l removal after breakthrough) was not fully understood. There were a few possibilities mentioned earlier with the presence of Mg^{2+} being the most likely theory. To test this theory fresh (preconditioned) clinoptilolite (0.9716g) was soaked in 477mg/l (477ppm) NH_4^+ for 7 days. The solution was then tested for Mg^{2+}, Ca^{2+}, and K^+, to see if Mg^{2+} or any other ions were responsible.

Table 6.2: Ionic concentrations.

	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}
Equilibrated concentration (ppm)	191	181	54	1	21

Table 6.2 shows that most of the ions present were NH_4^+ and Na^+ as would be expected; the other three should not have been present at all. Significant amounts of Ca^{2+} and K^+ were measured, and almost no Mg^{2+} was present after equilibration. Of the 4 sites in clinoptilolite M1 and M2 have a reasonable affinity for Ca^{2+}, and site M3 has a very high affinity towards K^+. Therefore it is possible that Ca^{2+} and K^+ are responsible rather than Mg^{2+} for the phenomena observed in Figure 6.2.

Table 6.2 is not representative of all the ions present in clinoptilolite and there may have been more Mg^{2+} than the 1ppm, which was released into solution. It does however show that K^+, and Ca^{2+} were present in significant quantities.

The service cycle and regenerant solutions contained no K^+, Ca^{2+}, or Mg^{2+} ions and eventually they were removed from the resin after a few runs. However in real industrial situations these ions will be present and may significantly reduce the capacity towards NH_4^+ removal, due to their high selectivity towards individual sites.

Figure 6.4 shows the breakthrough behaviour of clinoptilolite in the presence of citric acid. The result is similar to that observed in the absence of citric acid (see Figure 6.3). After one regeneration the bed life increased slightly, from ~230 bed volumes to ~270 bed volumes. This increase is only a 17% increase whereas in Figure 6.3 ("NH_4^+-only") the increase observed was 42% after one regeneration. As was the case in the absence of citric acid, figure 6.3 ("NH_4^+-only"), the amount of NH_4^+ removal after breakthrough occurs is reduced after each run. In Figure 6.3 ("NH_4^+-only") the breakthrough increased on each occasion to a maximum of around 460 bed volumes. In the presence of citric acid a maximum breakthrough of ~340 bed volumes was processed in run 4. After run 4 the breakthrough decreased to 300 bed volumes for run 5. Also the slope of the 2nd breakthrough curve is much steeper than the 1st.

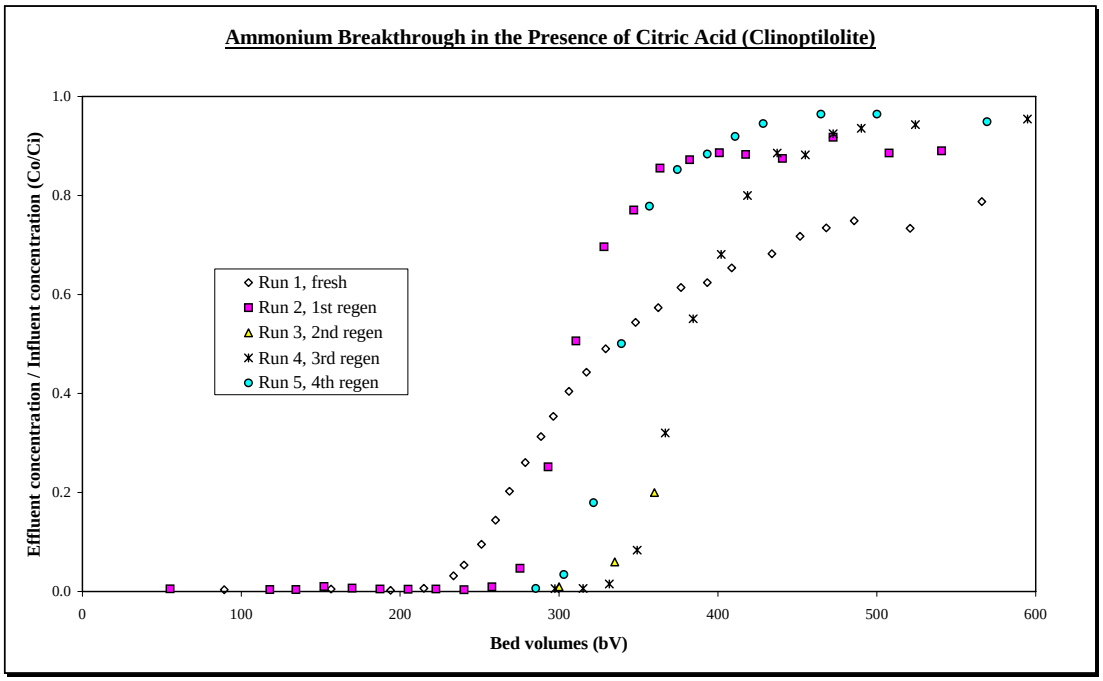


Figure 6.4: Ammonium ion breakthrough in the presence of citric acid in a column of clinoptilolite.

N.B. Run 3 was stopped shortly after breakthrough due to equipment failure. This did not affect the results of the data shown or any other experimental run contained within this report.

Acids may clean out impurities (especially CO_3^{2-}) out of the macropores of clinoptilolite and this may explain why the slope of the breakthrough curve dramatically increased from the first to second run, see Figure 6.4.

It is also known that acids can dealuminate zeolites and (the ratio of Si:Al in clinoptilolite is 5:1 [13,14,45]) the loss of aluminium from the structure will lower clinoptilolite's capacity for cations. However the physical structure can still exist because of its high silicon content. Zeolites with a higher ratio of aluminium can breakdown.

Zeolites with a high silicon to aluminium ratio also exhibit higher ion exchange kinetics, which is another possible explanation for the steeper slope in run 2.

The increase in capacity from run 1 to run 4 can be attributed to reasons discussed earlier for Figure 6.3. The increase in capacity was not as large as that observed for "NH_4^+-only" and actually decreased from run 4 to run 5. This is likely to be due to capacity loss as aluminium is lost from the crystal by the acids.

Previous studies using preconditioned clinoptilolite, determined that there was a loss of capacity, attributed to dealumination [16,45]. In this project a small sample of clinoptilolite was added to a pH 1.0 solution of HCl and bubbling was observed, suggesting a chemical reaction between the acid and compounds in the zeolite. This was accompanied by a change in colour from light brown to a near white colour.

Figure 6.5: Left is "NH_4^+-only", centre is NH_4^+/citric acid, right is fresh resin.

After the 5th run of "NH_4^+-only" and NH_4^+/citric acid it was noticed that each of the resins changed colour. As can be seen in Figure 6.5 the fresh resin on the right hand side is a light brown. The "NH_4^+-only" resin darkened, and the NH_4^+/citric acid resin went almost pure white. The whitening of the resin by NH_4^+/citric acid can be attributed to the acid.

Clinoptilolite did not obviously change colour as the ionic form changed, rather it changed colour slowly over the duration of 5 runs. The reasons for the colour change during the "NH_4^+-only" experiments is not known but structural changes to the clinoptilolite are a possibility requiring further investigation. This may go some way to explaining one of the earlier theories on why breakthrough extended and the removal after breakthrough disappeared.

Figure 6.6 shows the breakthrough results for ammonium uptake in the presence of glucose. There are similarities to the exchangers conducted in the presence of citric acid, and after regeneration, Figures 6.3 and 6.4. These showed in increase in the volume of water treated to breakthrough compared to the control. There was also a reduction in the amount of NH_4^+ removed well after breakthrough. These two observations are also seen in Figure 6.6.

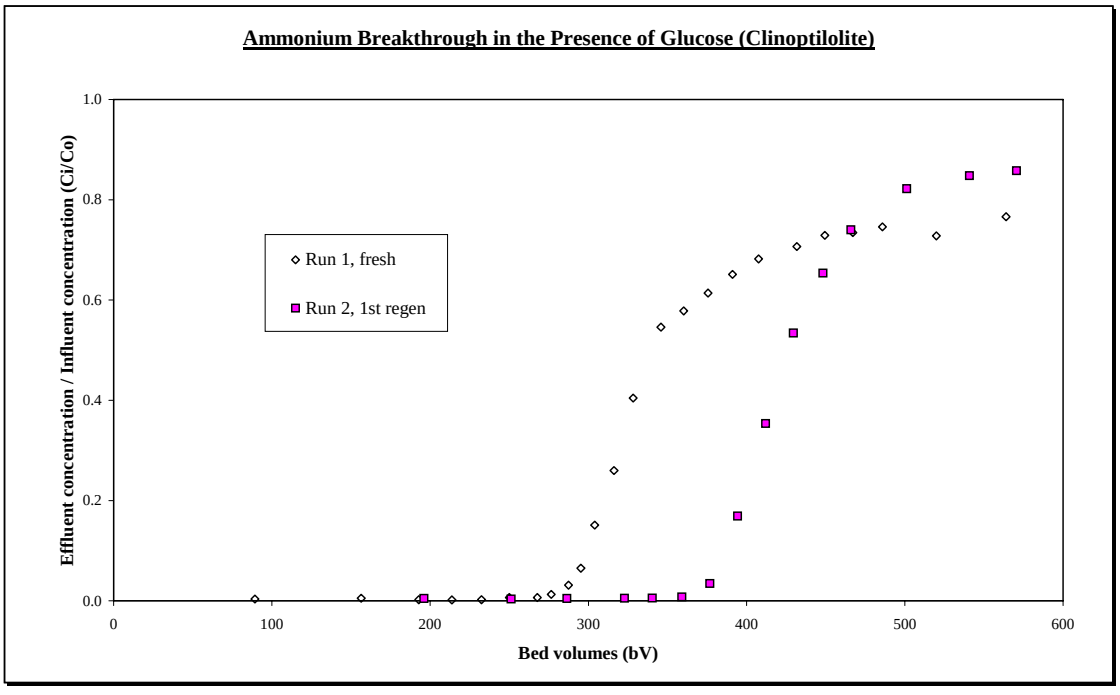


Figure 6.6: Ammonium ion breakthrough in the presence of glucose in a column of clinoptilolite.

After approximately 580 bed volumes the resin bed with NH_4^+/glucose began to swell up the column and some voids (channels) began to appear. The flow was then immediately halted by turning the pump off.

The solution and the resin were emptied from the column into a beaker and it was observed that upon gentle swirling of the solution that the resin and solution appeared to be very gelatinous and the particles appeared fluidised. The same steps were repeated for the other two columns ("NH_4^+-only" and NH_4^+/citric acid) and upon gentle swirling acted as expected, the water easily drained from the columns, they made a grinding noise as the granules scrapped by each other and they sat very firmly on the bottom under the water level.

In the layer of water above the resin (in the beaker) that had been treated with NH_4^+ and glucose there were a number of 'floaties', which were not present in the other two solutions. The solution was also more viscous. It was thought that biomass had been growing on the resin. The solution was then tested for proteins by the Lowry procedure to determine if biomass was present. In the solution containing glucose a protein concentration of 40mg/l – 50mg/l was found, and no proteins could be determined in the "NH_4^+-only" and NH_4^+/citric acid solutions.

It is hard to see in Figure 6.7 but a number of 'floaties' or gel like pieces can be seen with the naked eye, and the solution was very viscous. It was believed that heterotrophic microorganisms were present and the gel like texture was caused by excreted extracellular polysaccharides.

Figure 6.7: Sample from NH_4^+/glucose column.

The three images in figure 6.8 show a number of filamentous organisms (possibly fungi) found in the water from the NH_4^+/glucose column (magnification 50x). Whilst it was not determined if these were biomass there were many of them in the glucose solution but none in the other two solutions. The darker spots are fines of clinoptilolite.

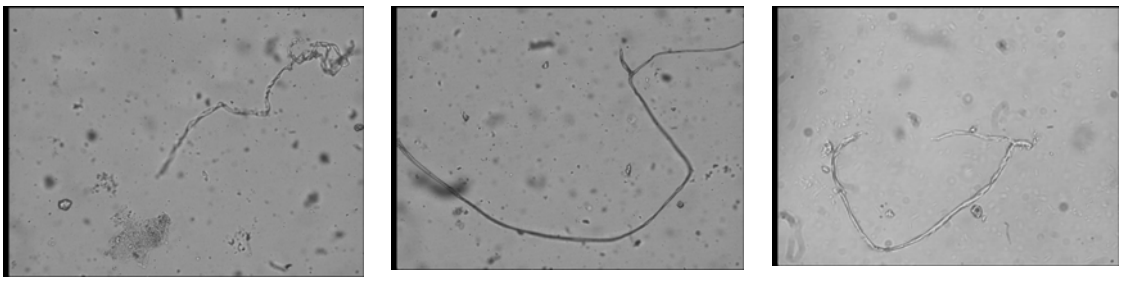


Figure 6.8: Filamentous microorganisms.

It would not be surprising if biomass was observed on the resin. It has been shown that clinoptilolite is a good solid support for bacteria [21]. The presence of glucose as a high energy carbon source, nitrogen from ammonia, the dissolved O_2 was approximately 9mg/l, and other minerals from the zeolite will supply the required nutrients for

growth. The zeolite was mined so the presence of trace amounts of other elements, which would tend to promote some biological growth, would be expected.

Proteins and filamentous organisms were found in the NH_4^+/glucose solutions in which microbial growth occurred. The columns containing "NH_4^+-only" and NH_4^+/citric acid showed no signs of microbial growth. During run two of each of the three columns dissolved O_2 levels were monitored. All three started at 9.0mg/l (O_2), NH_4^+/glucose dropped to 7.5mg/l, yet the other two DO_2 levels did not drop at all. This also suggests that there was no microbial growth in the "NH_4^+-only" and NH_4^+/citric acid columns. The DO_2 only dropped 1.5mg/l in the NH_4^+/glucose due to the high flowrate (residence time ~16mins). In the "NH_4^+-only" column nitrifiers are likely to grow over an extended period but at very slow growth rates, which is probably why none were detected. The low pH in the NH_4^+/citric acid column is probably why no microbes were present.

Prior to each run all tanks, tubes, columns etc. were sterilised with either sodium metabisulphite or bleach. The system was not totally sealed off from the environment, therefore some contamination can still occur during each run.

The growth of heterotrophic microbes was not the problem when glucose was present. It was the gel like substance (likely to be polysaccharides) that blocked the column. Regeneration of the column was not possible whilst the gel was present. Therefore during regeneration, the resin was removed from the column and washed in a series of batch steps with sodium dodecyl sulphate (anionic surfactant) to remove the gel. The gel needed to be removed otherwise it would prevent Na^+ ions from contacting the exchanger granules. It also channelled the solution through the column giving poor distribution.

The clinoptilolite was washed with distilled water to remove the sodium dodecyl sulphate and was then placed back into the column. Then regeneration continued as normal. The caustic solution would help sterilise the resin during regeneration. Each

regeneration also included a step with sodium metabisulphate to be sure sterilisation occurred.

The regeneration step described here, whilst not practical on an industrial scale, did work. This can be seen by the performance of the clinoptilolite in run 2. Plugging of the column did not occur until approximately 600 bed volumes of solution were processed, proving that most of the biomass was removed.

Removing the gel on a lab scale was very simple, however at commercial scale it would be much more difficult. Some ion exchange systems have a fluidisation step during the cleaning/regeneration cycle, however due to the brittle nature of clinoptilolite fluidisation is not possible. Pumping surfactants through would also not be practical, as the solution would only pass through the channels. Therefore the production of gels must not be allowed to form in the first place, possibly be having satisfactory BOD removal before ion exchange.

The presence of the gel could have caused problems with mass transfer, however a close look at Figure 6.1 shows that the breakthrough curve overlaps other NH_4^+/organic curves. It therefore does not appear to limit mass transfer, and hydraulic difficulties appear to be the only problem.

Another problem with heterotrophs is that they can inhibit nitrifying bacteria by competitively consuming dissolved oxygen. Nitrifying bacteria can be used in combination with clinoptilolite to enhance bed life and are required for biological regeneration [16, 18, 21]. One advantage of heterotrophic bacteria growth on clinoptilolite is that organics can be removed biologically at the same time as NH_4^+ is removed by ion exchange.

Figure 6.9, which shows the breakthrough results for ammonium ion uptake in the presence of phenol as the organic, indicates similar results to the other cases. The breakthrough extends for each run, and the removal after breakthrough diminishes.

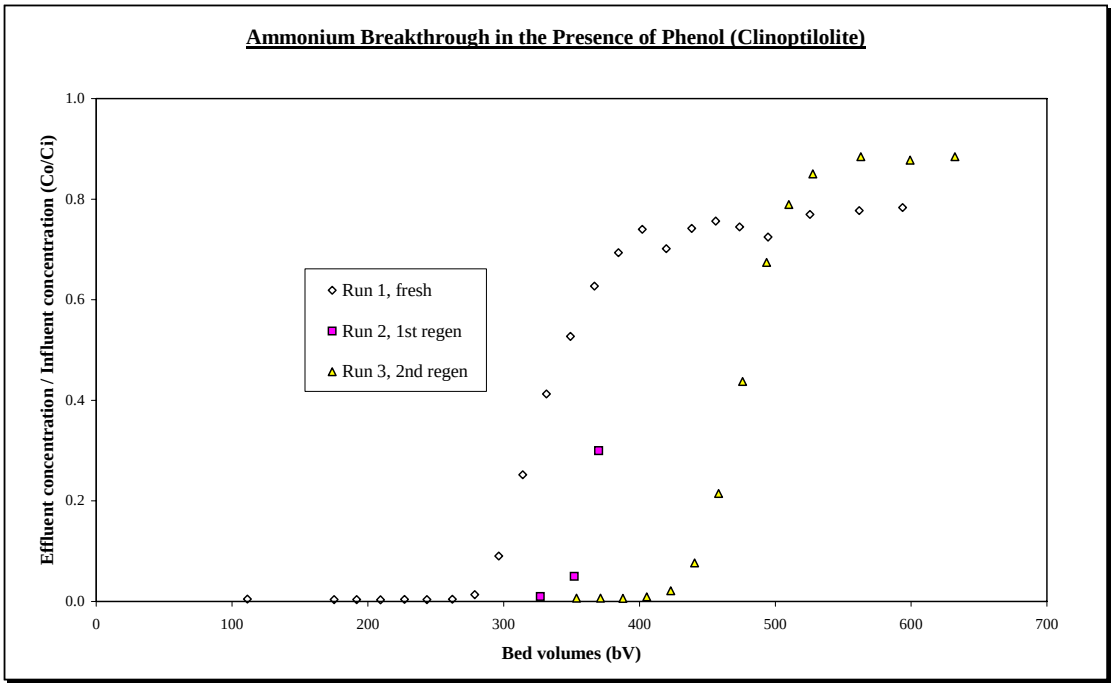


Figure 6.9: Ammonium ion breakthrough in the presence of phenol in a column of clinoptilolite.

There were no detectable signs of biological activity. This is likely to be due to the toxicity of phenol to many microbes. Phenolic compounds also inhibit nitrifiers [21].

Figure 6.10 shows ammonium ion breakthrough in the presence of sunflower oil. Results similar to those obtained for "NH_4^+-only" were obtained in the presence of hexane and sunflower oil. There was however a small amount of biological activity. Dissolved O_2 reduction was too small to detect, and no plugging of the column occurred. At the end of each run the tubing was removed from the column and the solution did not drain well suggesting the onset of plugging.

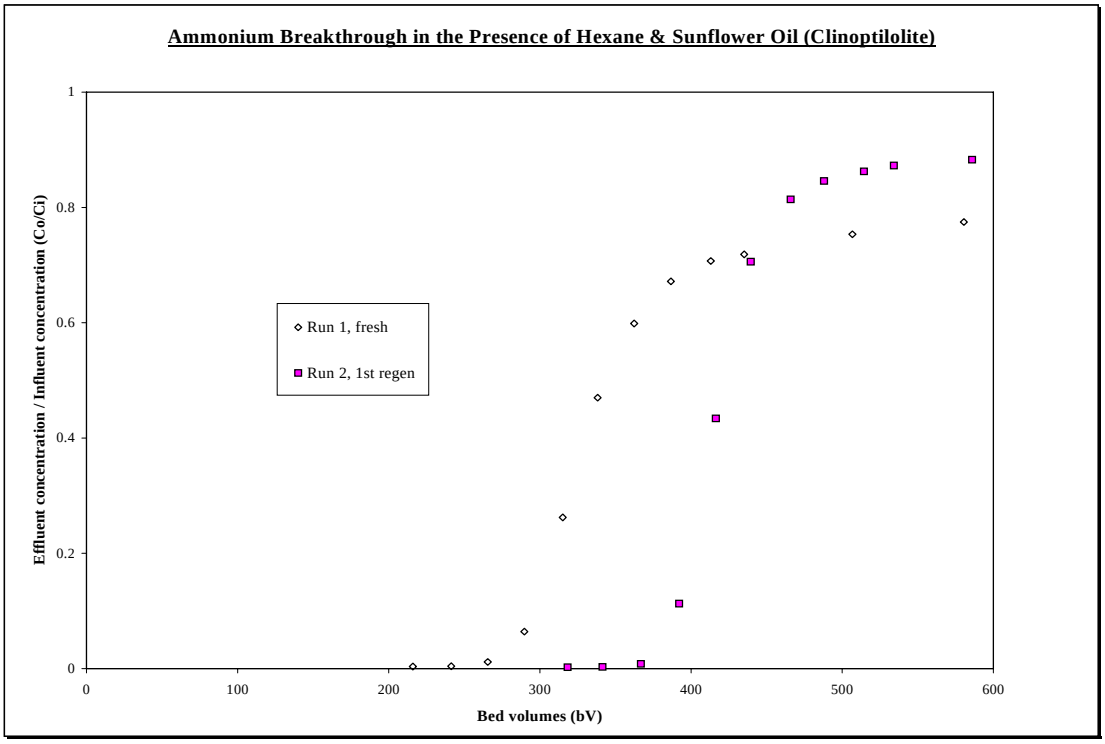


Figure 6.10: Ammonium ion breakthrough in the presence of hexane and sunflower oil in a column of clinoptilolite.

Proteins were tested in the study as they can cause problems with fouling of ion exchange resins. The breakthrough curves for Run 4 of the "NH_4^+-only" experiments (Figure 6.1) and that for the ion exchange of NH_4^+ in the presence of whey protein isolate (Figure 6.11) are comparable, but showing breakthrough after 450 bed volumes of water processed. Therefore just four cycles of exhaustion and regeneration the performance of clinoptilolite did not decrease. It would have been desirable to study the performance after a few hundred runs to determine if fouling had caused a loss in performance. This was not possible due to the length of time required.

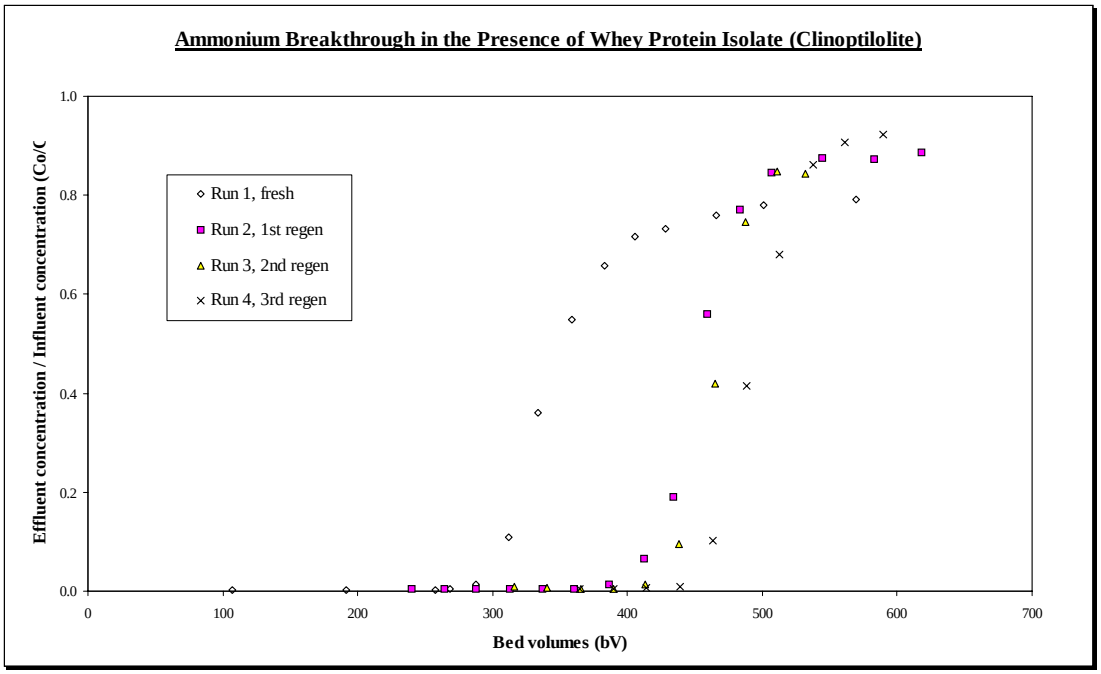


Figure 6.11: Ammonium ion breakthrough in the presence of whey protein in a column of clinoptilolite.

The results shown in Figure 5.3 showed that a small amount of whey protein was taken up onto clinoptilolite. However no significant adsorption of the whey protein was detected in the column of ion exchange since it was determined in the effluent shortly after the experiment was commenced.

The whey protein isolate (WPI) used comprised:

- 94Wt% - protein
- 5Wt% - lactose
- 1Wt% - various salts

Evidence of microbial growth was detected in the column during operation in the presence of whey protein isolate. This might be expected since the proteins and lactose present provide a mixture of carbon sources and trace amounts of salt necessary for

microbial growth. The growth was not as rapid as in the case of glucose was used however it was significant enough to cause plugging after approximately 650 bed volumes.

At this point a tracer experiment was conducted to determine the mean residence time. An approximate residence time was noted which compared with a value of 12 minutes based on ideal flow. The production of polysaccharides possibly had reduced the void space in the packed bed thus reducing the residence time of solution. This indicated significant biological growth in a short time in the presence of 20mg/l of organic material. The tubing was removed from the column upon which solution drained from the column extremely slowly thus showing that the column was severly blocked. The resin was visibly examined and showed a gel like texture, similar to that observed in the case of the glucose experiment.

Of the organics used in the column studies the glucose was associated with the most rapid plugging of the packed bed. The presence of whey protein also produced significant obstruction. Real wastewaters contain a wide mixture of dissolved organics, including various surfactants. The presence of various organics appears to be associated with plugging of the packed bed and the production of polysaccharides is a likely explanation.

Two column experiments were linked together. One column was fed with NH_4Cl and glucose, the other fed with NH_4Cl, glucose and whey protein. The whey protein is very surface active and it was possible that polysaccharides would be removed even though it could act as an additional substrate for microbes.

The NH_4^+/glucose/WPI column began to expand after 350 bed volumes, and the NH_4^+/glucose column after 650 bed volumes. Therefore the presence of the WPI actually caused the column to plug at an earlier stage, yet in a different manner to previous experiments. All previous columns with an organic present formed cracks

and voids to channel the solution. Yet the NH_4^+/glucose/WPI column evenly expanded and appeared fluidised.

Once the NH_4^+/glucose/WPI column had expanded dye was injected at the inlet. The dye could be seen jetting up the walls inside the column and exited at the wall. The dye began emerging 2.5 minutes later compared with 12 minutes residence time observed with fresh clean resin.

After 450bV of solution was passed through the NH_4^+/glucose column, dye was injected and exited 6 minutes later, which compared unfavourably with the initial 12 minutes. After 600bV dye exited 2.5 minutes later. Once the column started breaking apart after 700bV the dye took 2.5 minutes to exit and could be seen to be passing between the packed bed and the walls. Once columns became plugged the flow of the dye suggested that the solution passed between the resin and the wall.

Figure 6.12 shows a bed of clinoptilolite disrupted by plugging with polysaccharides. The organic used in this experiment was whey protein. A horizontal gap of approximately 10mm was typical of that observed when break-up of the bed was observed. The gap usually formed at the base of the packed bed, rather than in the middle as shown in Figure 6.7. At the end of the first run of glucose the gaps were vertical and diagonal. In all other cases they were horizontal.

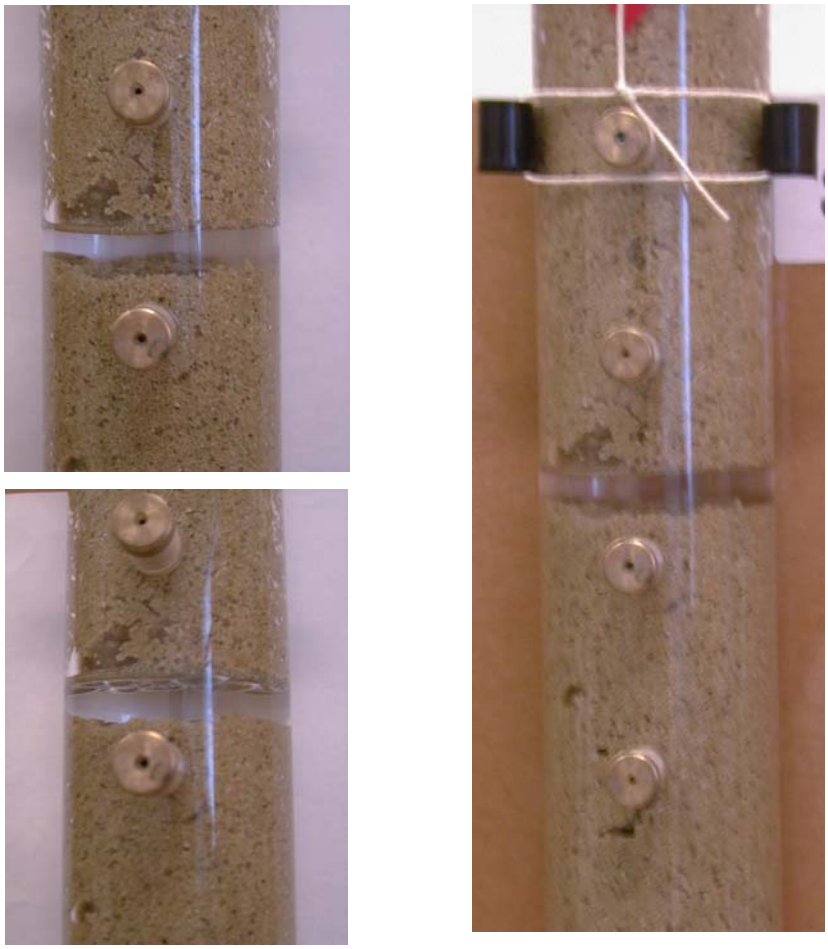


Figure 6.12: Clinoptilolite bed plugged with biomass.

Dissolved oxygen levels were monitored during each run involving clinoptilolite. There was no decrease in dissolved oxygen from the inlet to the outlet except for when WPI, glucose, WPI/glucose were present. No detectable decrease in dissolved oxygen was observed when hexane/sunflower oil were present, even though there were signs of microbial activity.

Table 6.3 shows that the experiments in which whey protein and glucose were present together experienced the largest dissolved O_2 decrease. Glucose would have provided the bulk of the carbon and the whey protein other nutrients. The experiment involving whey protein alone experienced the smallest dissolved O_2 drop, which is partially due to the WPI concentrations being significantly lower than glucose on its own. All of the

dissolved O_2 decreases are low and are due to the high flowrate, hence low residence time.

Table 6.3: Dissolved O_2 levels.

	Inlet O_2	Outlet O_2	O_2 decrease (mg/l)
Glucose	9.0	7.5	1.5
Whey protein isolate	9.0	8.0	1.0
Glucose and whey protein isolate	9.0	7.0	2.0

The dissolved O_2 drop was constant for each run even though biological growth occurred. This is surprising given that increase in biomass may be equated to result in high levels of oxygen consumption. The increased numbers of microbes should increase dissolved O_2 consumption.

In Chapter 4.0 a number of batch equilibrations were discussed. In each case the presence of an organic showed significant enhancement for the uptake of NH_4^+. By contrast in the column studies the only uptake enhancement was very small (see Figure 6.1), and in one case (citric acid) there was a slight decrease in capacity. One difference between the batch and column studies was the presence of Na^+ in solution in the batch experiments, where once sodium was released from the clinoptilolite it remained in solution and participated in the equilibrium.

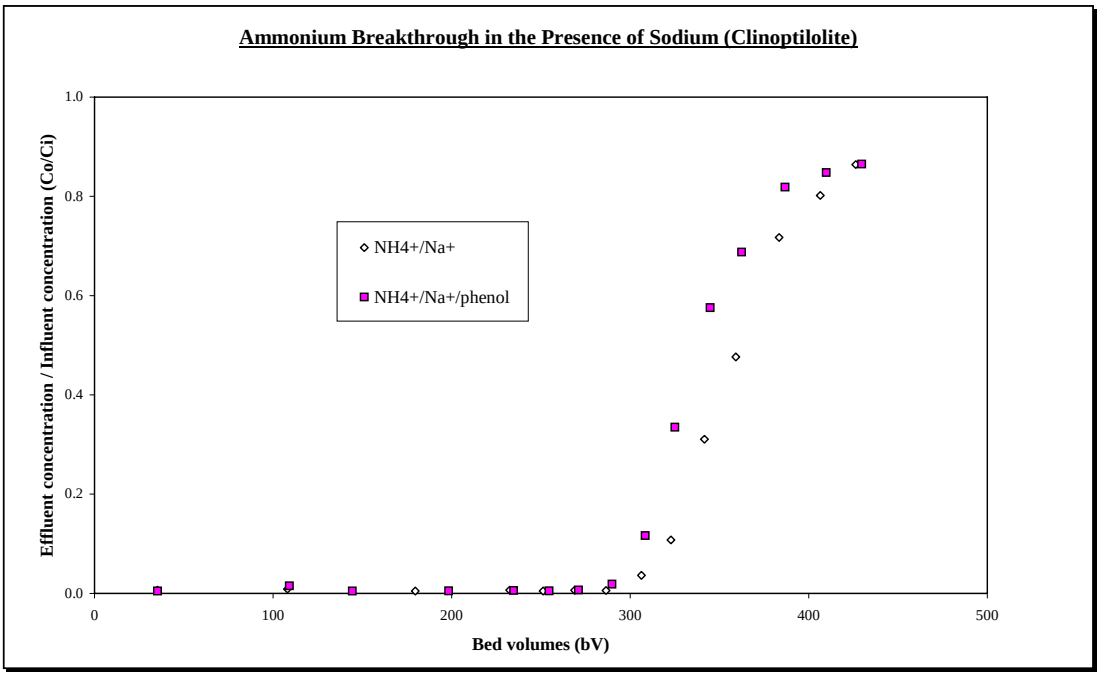


Figure 6.13: Ammonium ion breakthrough in the presence of sodium and phenol in a column of clinoptilolite.

It is possible that the presence of sodium ion in the zeolite may affect the way in which the organic contaminant influences the ion exchange capacity and selectivity. Therefore some Na^+ ions may remain in the clinoptilolite where the presence of the organic can displace more Na^+ hence enhancement can occur. In the column however all the Na^+ is expelled from the column and the released Na^+ ions are flushed away leaving the resin fully in the NH_4^+ form. If the resin is totally in the NH_4^+ form then it is possible that enhancement may not occur, as there are no Na^+ sites left for enhancement to occur at.

This hypothesis was tested by setting up two columns. One containing NH_4^+/Na^+ and the other NH_4^+/Na^+/phenol, the run without phenol was used as a control. Phenol was chosen as it enhanced NH_4^+ uptake in the batch study, and because microbial growth was inhibited in the presence of phenol. The Na^+ was present in the influent at a concentration of 100ppm Na^+ as NaCl.

The results can be seen in Figure 6.13 and show that the presence of the phenol appeared to cause an earlier breakthrough. This may have been expected if fouling of the exchanger due to the presence of an organic had occurred. However the result presented in chapter 4.0 and with earlier results in this chapter, which showed enhancement in the presence of an organic.

6.2 POLYMERIC EXCHANGER BREAKTHROUGH CURVES

In the case of the column breakthrough experiments involving Dowex 50w-x8, there were significant hydraulic problems caused by the accumulation of small gas bubbles in the bed of the exchanger. Eventually the bubbles expanded and caused discharge of resin into the liquid effluent stream. The expansion of the bed was not caused by fluidisation of the low-density resin because its falling velocity was much higher than the solution velocity. Reasons for the bubble formation were not known as the solutions were heated initially to remove excess dissolved oxygen. However bubble formation was not observed during the NH_4^+/WPI experiments.

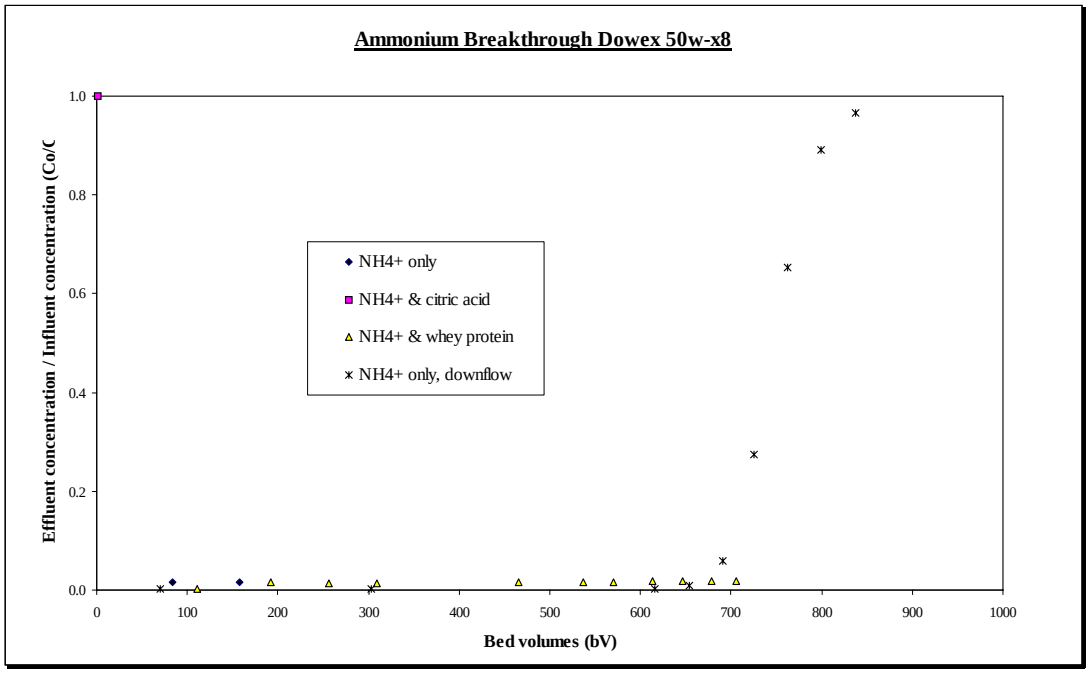


Figure 6.14: Ammonium ion breakthrough in a column of Dowex 50w-x8.

Following the feed of 710 bed volumes through the column in the presence of NH_4^+/WPI expansion of the bed was observed. This was observed not to be due to gas bubbles but due to biomass growth, hence the experiment was discontinued before breakthrough occurred.

Due to these problems with bed expansion the equipment was reconfigured to allow one downflow experiment in the presence of "NH_4^+-only". The results are shown in Figure 6.14.

In the case of clinoptilolite, the outlet NH_4^+ concentration, prior to breakthrough, was less than 0.1mg/l. Outlet concentrations, prior to breakthrough, from the upflow Dowex 50w-x8 experiments were in the range 0.7-0.9mg/l. When the Dowex 50w-x8 column was run in the downflow direction the concentration of NH_4^+ in the effluent was less than 0.1mg/l.

Figure 6.15 shows the breakthrough curves for various solutions treated on columns of fresh (preconditioned) Purolite MN500. The presence of whey protein appears to have no effect on the uptake of NH_4^+. The presence of citric acid competitively competes for sites with H^+ ions causing a significant decrease in capacity until breakthrough. This observation was also seen in the batch experiment (see Figure 4.18).

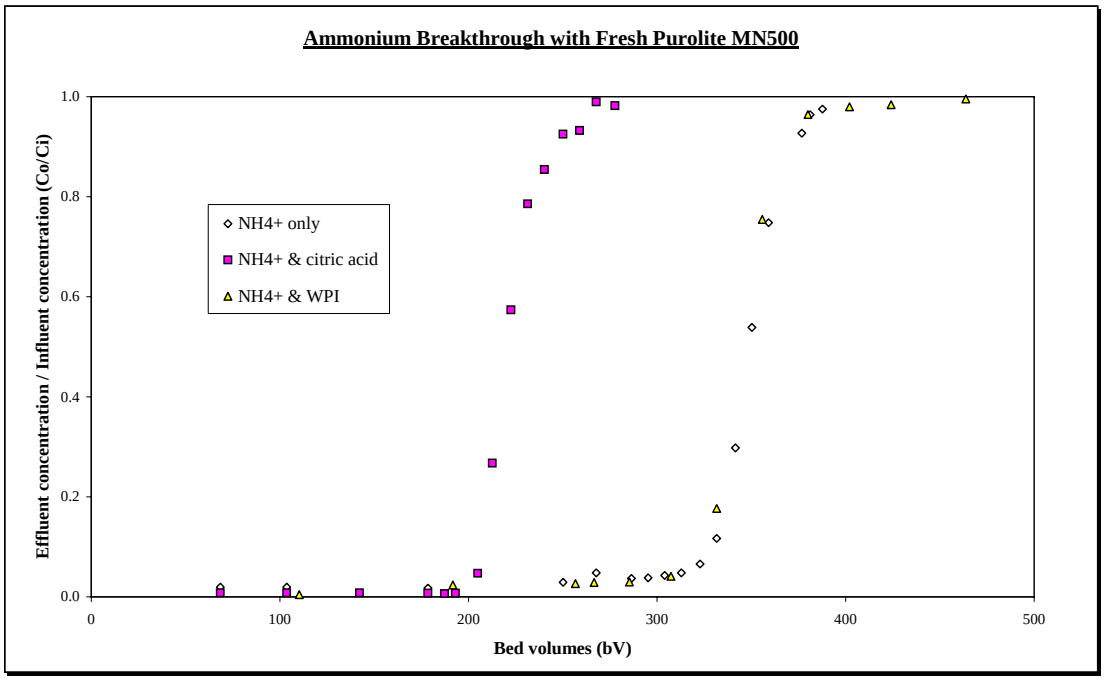


Figure 6.15: Ammonium ion breakthrough in a column of fresh Purolite MN500.

Unlike clinoptilolite the slope of the breakthrough curve in the presence of citric acid (onto MN500) is the same as in the case of the "NH_4^+-only" onto MN500. NH_4^+ uptake in the presence of citric acid onto clinoptilolite yielded a breakthrough curve with a low slope relative to "NH_4^+-only" (see Figure 6.1).

In the case of MN500, after breakthrough no further removal of NH_4^+ ions was observed which contrasted with clinoptilolite. In the case of clinoptilolite after breakthrough 20% of the influent NH_4^+ ions were still being removed.

The other difference observed between clinoptilolite and Purolite MN500 was the degree of removal attained before breakthrough. Clinoptilolite was able to polish the effluent to below 0.1mg/l. MN500 was not able to polish the water to such a low specification. Effluent concentrations for "NH_4^+-only" onto MN500 varied between 0.9mg/l - 1.9mg/l. Just before breakthrough occurs there is a small ramp increase in the effluent concentration up to ~2.5mg/l.

Whilst MN500 is able to remove most of the influent NH_4^+ ions, the amount passing through can be significant. In the case of wastewater treatment for discharge, such effluent may be acceptable, but it would be perhaps unacceptable in the case of water for recycle or re-use such as in aquaculture. Depending on the type of fish species present NH_4^+ concentrations of 0.5mg/l – 2.5mg/l [16] are not usually acceptable.

Data shown in Figure 6.3 showed that after one regeneration the column of clinoptilolite displayed a significant increase in its capacity. For the case of "NH_4^+-only" onto MN500 the same is not true and no change in exchange capacity was observed after one regeneration, see Figure 6.16.

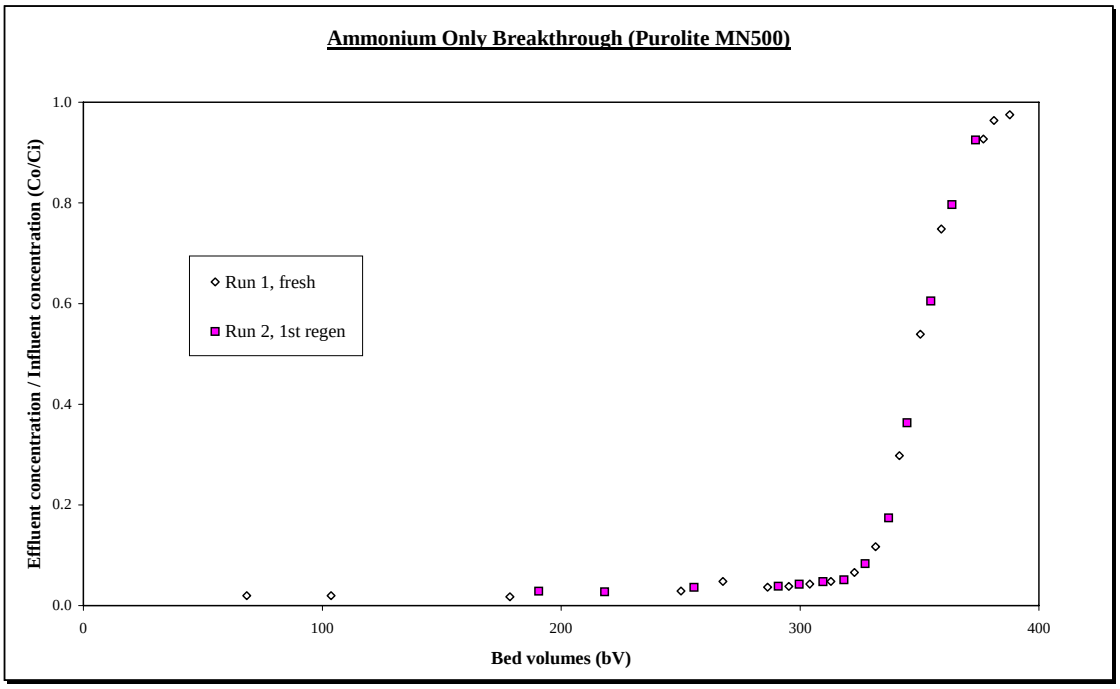


Figure 6.16: Ammonium ion breakthrough in a column of Purolite MN500.

Clinoptilolite contains 4 different sites within each crystal. Purolite MN500 has sites randomly dispersed throughout the matrix of the resin. Also Ca^{2+}, Mg^{2+}, and K^{+} were not present in the case of MN500 to cause the increased capacity until breakthrough as was seen with clinoptilolite.

The data in Figure 6.15 show that the presence of citric acid caused a significant decrease in the capacity for NH_4^{+} ions onto Purolite MN500. In contrast the results in Figure 6.4 for clinoptilolite show almost no loss in capacity when citric acid is present. This may be explained by the two exchangers each having a different selectivity for H^{+} ions.

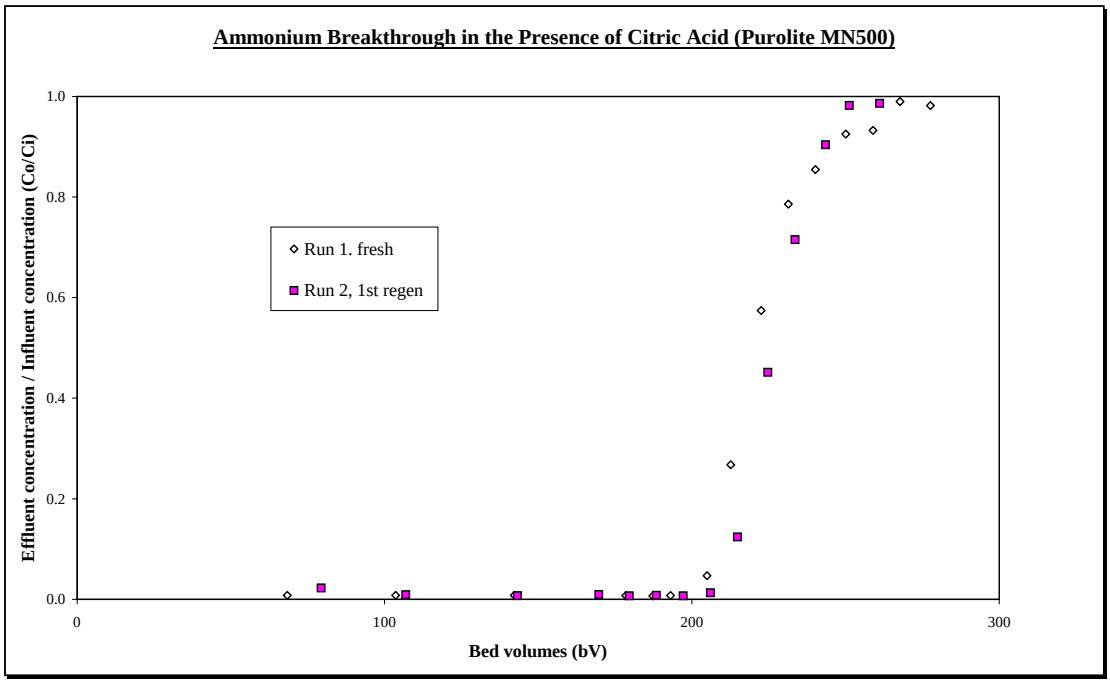


Figure 6.17: Ammonium ion breakthrough in the presence of citric acid in a column of Purolite MN500.

Whilst MN500 showed a reduced exchange capacity in the presence of citric acid, it is apparently not damaged or modified by exposure to a low pH environment. Zeolites may be damaged at low pH due to the possible removal of aluminium. Hence the performance of the MN500 resin is not significantly reduced after a number of regenerations.

Proteins are known to foul various types of ion exchangers; hence a number of runs and regenerations in the presence of whey protein isolate were carried out. The results are shown in Figure 6.18 and a small decrease in capacity from run 1 to run 4 is observed. Fouling or the presence of bubbles in the packed bed could cause this. The effect of fouling by whey protein over the long term could not be determined in this project because of the long times required.

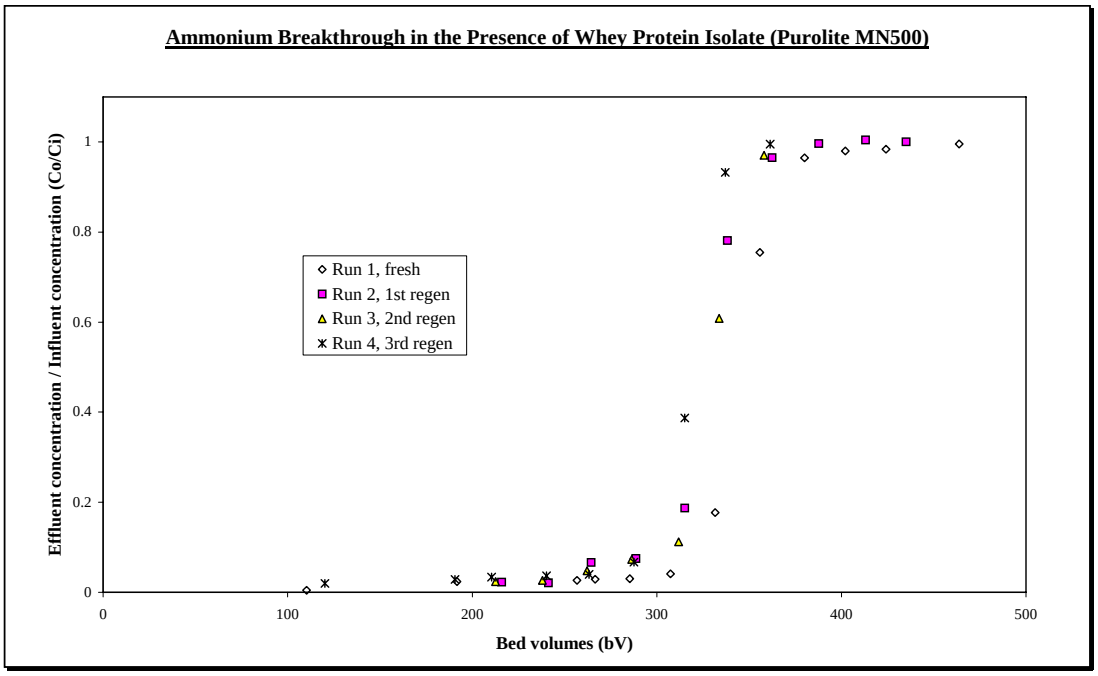


Figure 6.18: Ammonium ion breakthrough in the presence of whey protein in a column of Purolite MN500.

The presence of biomass growth was a problem in the presence of whey protein, just as it was in the case of clinoptilolite. The packing also began to break-up as the void spaces filled with polysaccharides. Although MN500 runs were shorter than clinoptilolite plugging still occurred due to the lower density of MN500. This made it easier to lift the packed bed of MN500.

At the end of those runs where significant polysaccharide production was suspected, samples of the resin (both clinoptilolite and MN500) were removed from the column. These were examined under a scanning electron microscope and no bacteria could be found on the surface of the exchanger. Therefore it is possible that the only microbial material present was in the filamentous form.

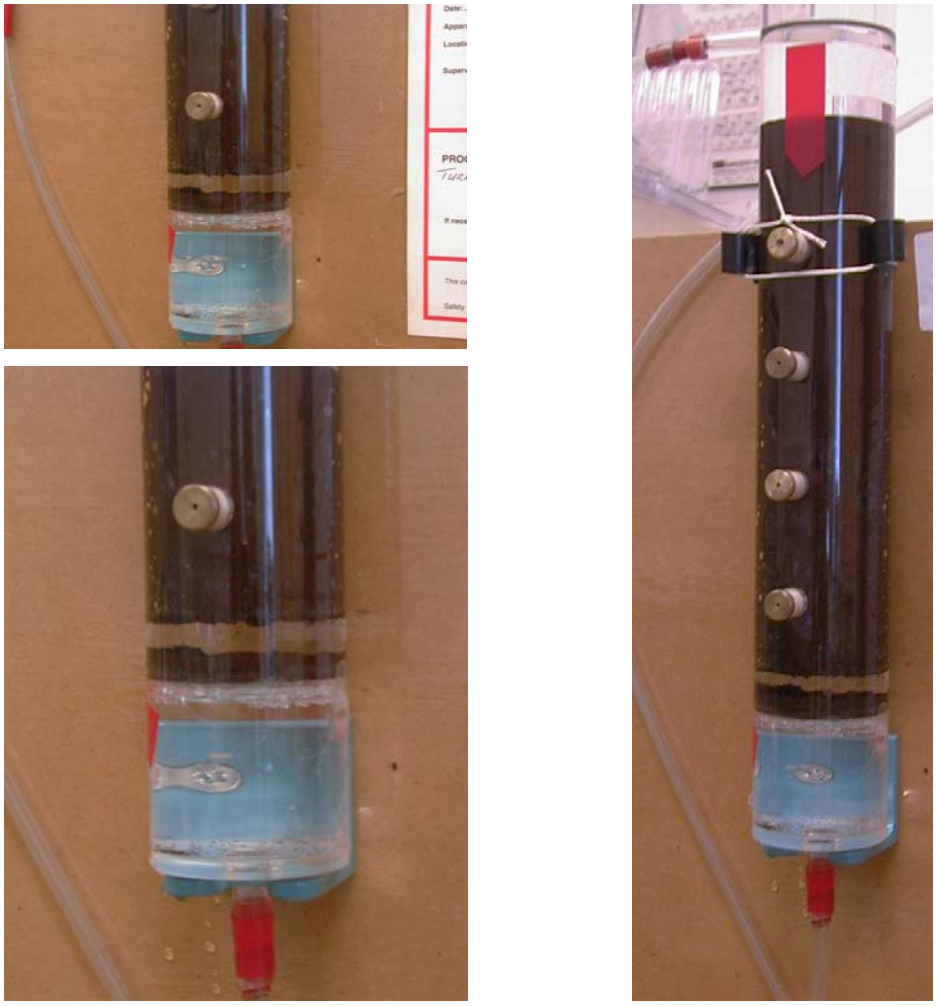


Figure 6.19: Purolite MN500 bed plugged with biomass.

6.3 RESIN COMPARISON

Figure 6.20 shows the results of a number of different "NH_4^+-only" runs onto the three exchangers. Dowex 50w-x8 showed the largest capacity. Clinoptilolite capacity varied depending upon regeneration history and hence results from run 1 and run 5 (Figure 6.3) are both shown. Purolite MN500 showed a lower capacity but it gave the sharpest breakthrough.

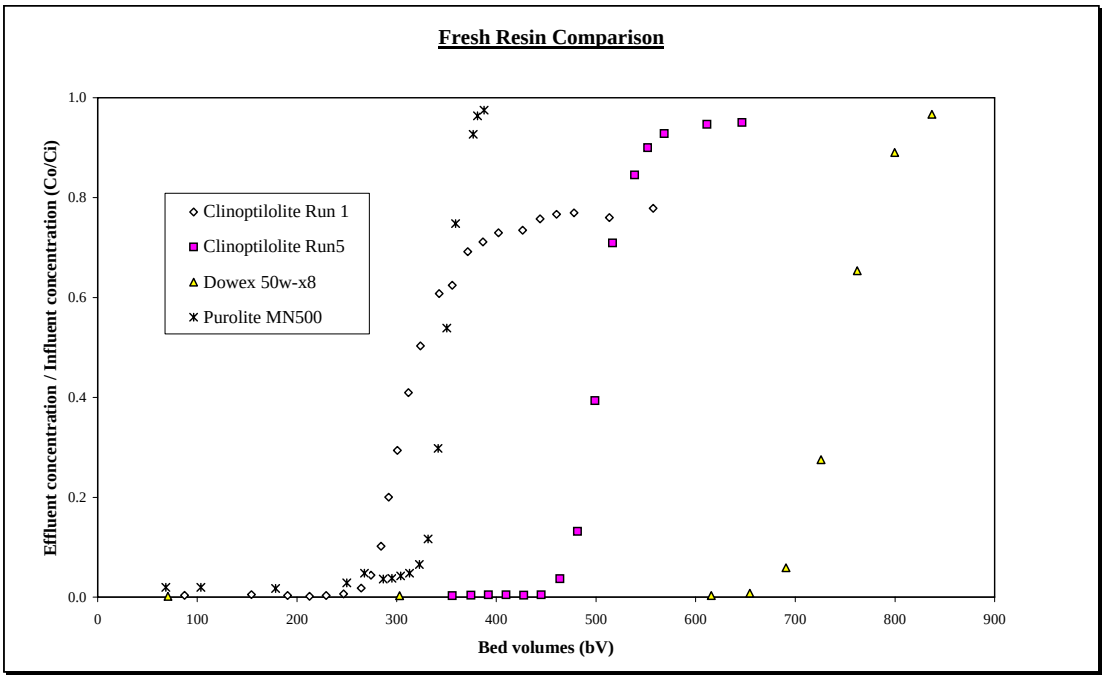


Figure 6.20: Ammonium breakthrough onto each of the three resins.

6.4 DISCUSSION COLUMN STUDIES

The presence of a number of organic compounds were studied in NH_4^+ removal by packed columns. In each case the organic appears to have almost no effect on the ion exchange of NH_4^+. The only possible problem appears to be the production of polysaccharides by heterotrophic microbes. In an actual treatment process real wastewaters are likely to contribute to BOD and since organic contaminants would also need removal it would be necessary to put organic removal prior to the ion exchange columns. Organic removal could be carried out using biological treatment or activated carbon systems.

Another possibility would be to add an antimicrobial agent such as sodium metabisulphite ($Na_2S_2O_7$). However it would also add cost to the process and inhibit biological treatment in other stages, and may itself be undesirable.

Only a few regenerations were carried out and there were no signs of the resins losing their performance, except in the presence of citric acid on clinoptilolite. Though under most real situations it is unlikely that the pH would be as low as was used in this experiment. Determination of long term fouling of resins by organics is something that would take a long time, which was not possible for this project.

Each column was run at one flowrate (3bV/hr), one inlet NH_4^+ concentration (50mg/l), and individual organics at one concentration each. It would have been useful to examine each variable in further detail but time was constrained. The effect of flowrates can be studied by modelling with the bed depth service time model.

Prior to breakthrough clinoptilolite was able to reduce the concentration of NH_4^+ to less than 0.1mg/l NH_4^+. Dowex 50w-x8 and Purolite MN500 in the upflow direction did not perform well. However in the downflow direction Dowex 50w-x8 was able to polish the water to less than 0.1mg/l NH_4^+. This suggests that the two polymeric resins do not pack as well as the heavier clinoptilolite. This results in a small amount of NH_4^+ (0.7mg/l – 2.5mg/l) reaching the effluent prior to breakthrough.

7.0 KINETICS, RESULTS & DISCUSSION

In chapters 4.0 and 6.0 the results of the studies of the equilibria and column breakthrough behaviour for the removal of ammonia were presented and discussed. In this chapter the kinetics of NH_4^+ uptake are discussed. The work compared the uptake rate of NH_4^+ onto the three different ion exchange resins and investigated if the presence of organic compounds changed the rate of uptake. The solutions used and their concentrations are examined in Table 7.1.

Table 7.1: Pollutant concentrations.

COMPOUND	**CONCENTRATION**
NH_4^+	50mg/l (0.148g/l NH_4Cl)
Citric acid	50ppm (0.533g/l)
Phenol	50ppm (0.261g/l)
Whey protein isolate (WPI)	10mg/l

7.1 UPTAKE RATE OF EACH RESIN

The results in Figure 7.1 show that Dowex 50w-x8 gave the fastest rate of exchange. Based on the breakthrough data it was initially expected that Purolite MN500 would be the fastest to reach equilibrium. Dowex 50w-x8 was expected to be the slowest, and clinoptilolite somewhere in between.

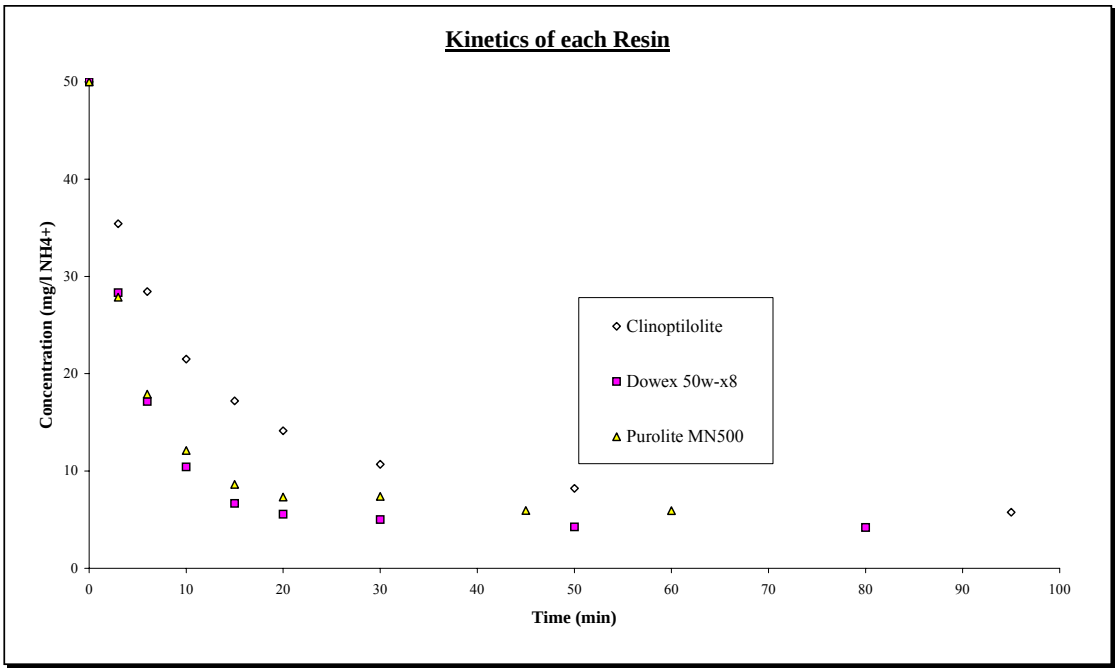


Figure 7.1: Uptake rate of three ion exchange resins of "NH_4^+-only".

The particle sizes of the three exchangers used in the experiments were the same as those used in the column studies. Despite Dowex 50w-x8 having little or no macroporosity it showed fast kinetics due to it having the smallest particle size of the three exchangers. The reason for Dowex 50w-x8 having a breakthrough curve with a low slope yet high kinetics could be a result of the high capacity.

7.2 UPTAKE RATE IN THE PRESENCE OF ORGANIC COMPOUNDS

The results in Figure 7.2 for clinoptilolite show that the presence of the organic has little effect on the rate of uptake. In the presence of citric acid there is a slight reduction in the uptake rate. However this could be attributed to the lower driving force due to the lower capacity, rather than the presence of the organic slowing kinetics perse (i.e. the ΔC is less hence less driving force).

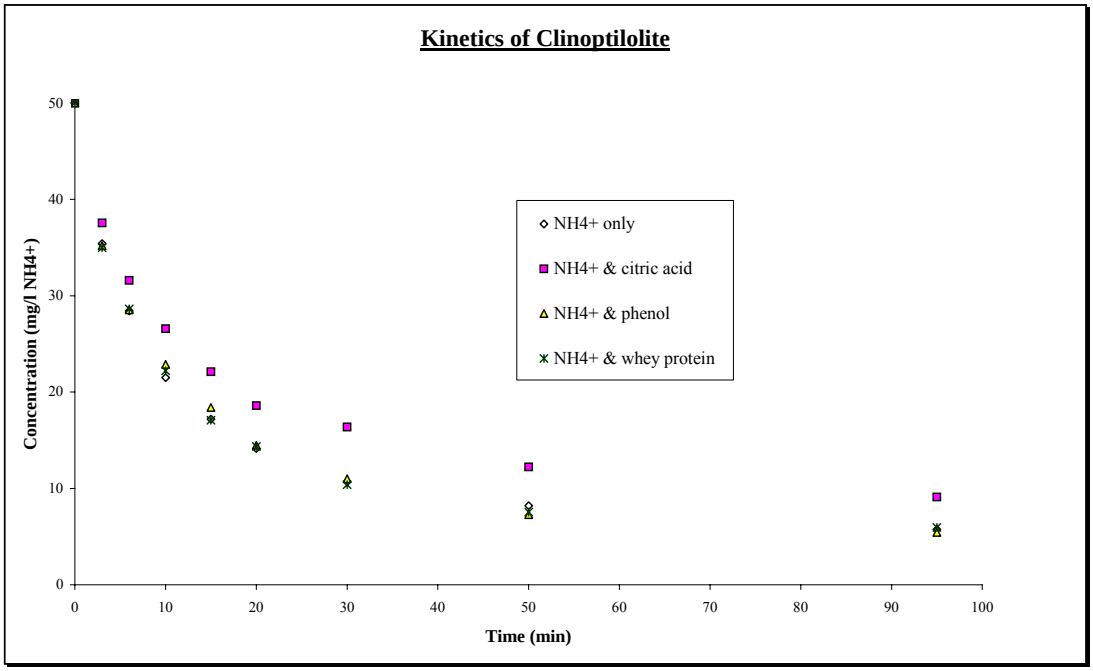


Figure 7.2: Uptake rate onto clinoptilolite.

The results for Purolite MN500 are shown in Figure 7.3. The presence of organic compounds also has a negligible effect on the uptake rate of NH_4^+ onto Purolite MN500. There is a very small reduction of uptake rate in the presence of citric acid due to there being a slight loss in capacity.

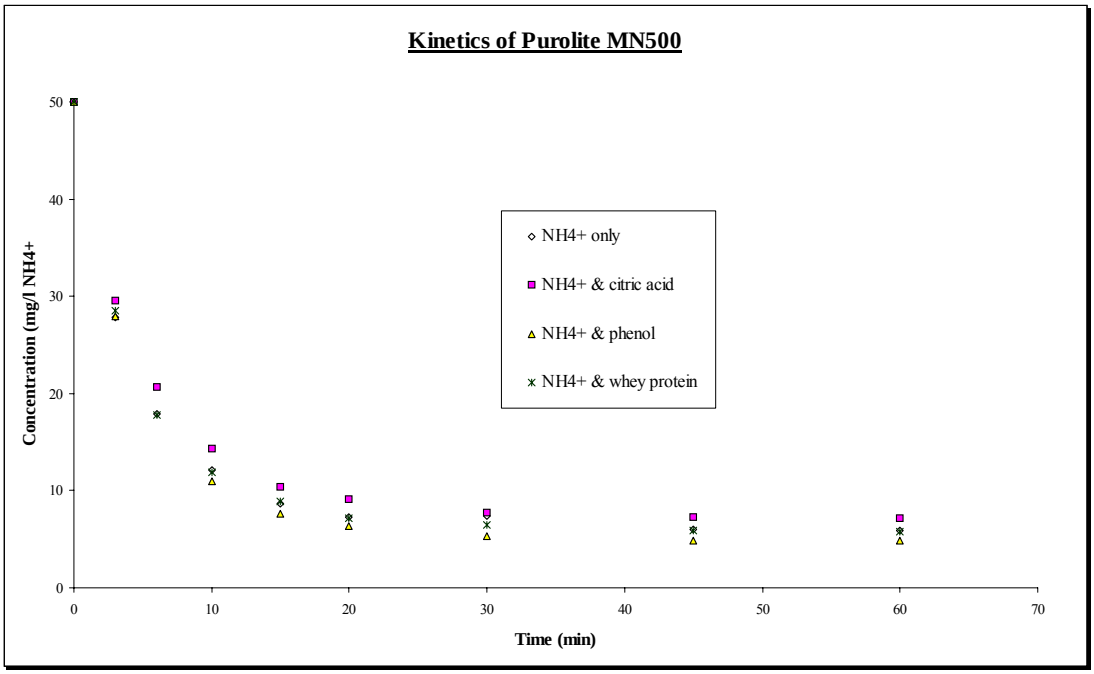


Figure 7.3: Uptake rate onto Purolite MN500.

Kinetic experiments with various organic compounds were not carried out on Dowex 50w-x8.

7.3 MODELLING OF THE UPTAKE RATE

The kinetic models referred in section 1.2.1.5 were fitted to the experimental data of NH_4^+ uptake onto clinoptilolite (see Figure 7.4). The Elovich model and the parabolic model fit reasonably well. The 1st order and modified Fruendlich models are less satisfactory. The Elovich model fitted well for the first 20 – 30 minutes; however it then deviated below the experimental data.

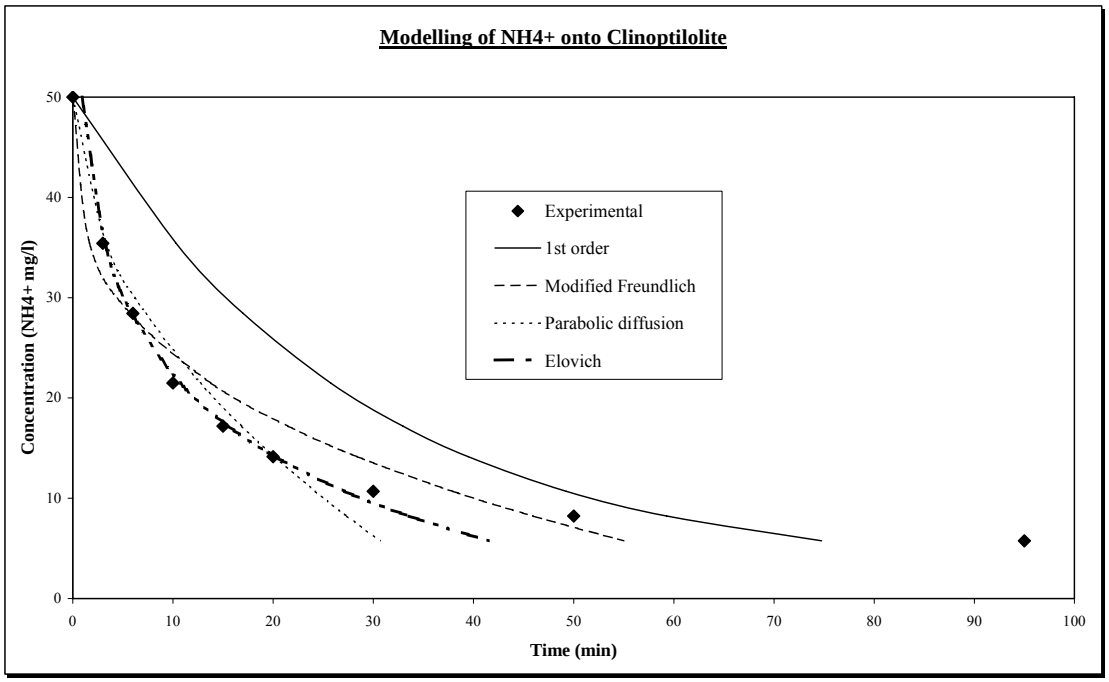


Figure 7.4: Kinetic models of NH_4^+ onto clinoptilolite.

Similar comparisons were made in the case of Purolite MN500 and the results are shown in Figure 7.5. In this case the Elovich model and the Modified Fruendlich model provide a reasonable fit to the data. The 1s order model and Parabolic diffusion models are less satisfactory.

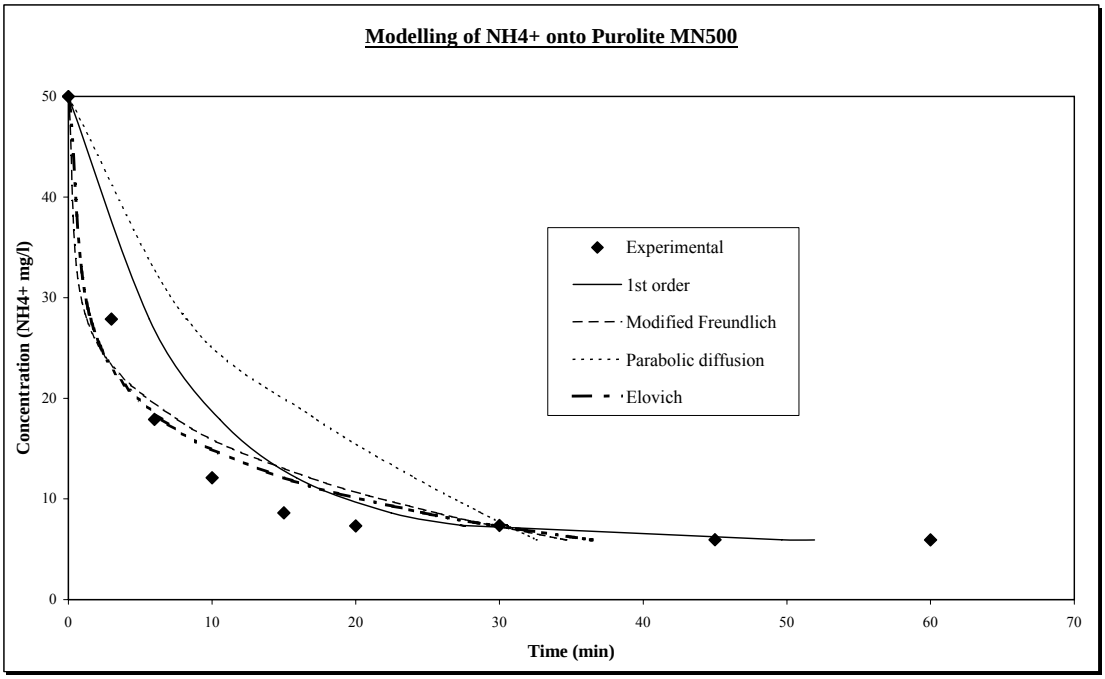


Figure 7.5: Kinetic models of NH_4^+ onto Purolite MN500.

8.0 CONCLUSIONS

8.1 BATCH EQUILIBRATIONS (CHAPTER 4.0)

A range of organic compounds were studied in the batch experiments and in each case there was significant enhancement of NH_4^+ uptake onto clinoptilolite at equilibrium. There was a little enhancement onto Purolite MN500 and no net enhancement onto Dowex 50w-x8. The reasons for the enhancement of NH_4^+ onto clinoptilolite are not fully understood. It is however possibly due to changes in the surface tension allowing for better access into the macropores of the resin. Ion exchange in the presence of the surface active proteins was enhanced, and thus could be explained by enhanced surface tension effects or possibly due to changes within the exchanger.

- The two exchangers with macropores showed enhancement, whereas Dowex 50w-x8 which has no macropores showed no enhancement.

- Dowex 50w-x8 showed the largest capacity for NH_4^+, and the other two exchangers showed lower capacities.

- Purolite MN500 showed a higher selectivity for NH_4^+ over Na^+ compared to clinoptilolite.

Ion exchange of ammonia from actual wastewater (woolscour waste water) showed complex behaviour. Therefore before installing an ion exchange plant pilot testing of real wastewater is critical to ensure correct design of plant.

8.2 ADSORPTION (CHAPTER 5.0)

Zeolites are useful gas phase adsorbents however they showed poor performance in the liquid phase of the three compounds studied. Some proteins were removed and it is therefore possible that clinoptilolite is a selective adsorbent. AFM, Dowex 50w-x8, and Purolite MN500 also showed little or no ability to adsorb aromatics or proteins. Activated carbon showed very high removal capacities for all compounds studied.

8.3 PACKED COLUMNS (CHAPTER 6.0)

There was negligible enhancement of NH_4^+ uptake onto clinoptilolite in columns, even when Na^+ was present in the influent. Organics appeared to have very little effect on any of the three exchangers used except growth of microbes and the possible production of polysaccharide gels was produced by their presence. The presence of surface-active proteins did not help the removal of polysaccharides out of the column plugging was still observed. The only problem appears to be the plugging of the bed causing hydraulic difficulties.

The presence of other cations (K^+, Mg^{2+}, and Ca^{2+}) appeared to be the cause of the increase of solution treated until breakthrough occurred and the removal of NH_4^+ after breakthrough.

8.4 KINETICS (CHAPTER 7.0)

A comparison of the uptake rate of each ion exchange resin (see Figure 7.1) showed higher exchange rate in the two polymeric resins. This could be explained by differing diffusion rates and slight differences in particle size.

The results from Figures 7.2 and 7.3 showed that the presence of an organic compound did not slow diffusion onto clinoptilolite of Purolite MN500.

8.5 GENERAL CONCLUSIONS

All three ion exchange resins performed well, yet in different ways. Dowex 50w-x8 had a very high capacity. Purolite MN500 showed high kinetics and is reported to be resistant to fouling and easy to wash. Clinoptilolite performed well and is the cheapest of the resins. None of the three resins were immune to bed plugging from polysaccharides. Clinoptilolite was degraded by citric acid; hence it should not be used in wastewaters with a low pH, whereas Purolite MN500 was not degraded.

9.0 RECOMMENDATIONS

- All organics were studied individually in this project. The example with real woolscour wastewater at the end of chapter 4.0 showed that there are interactions in complex mixtures. Future work could include studying the interactions of multicomponent systems to gain a better understanding to be able to make predictions. Until then pilot scale testing is required for new plants to prevent surprises after construction.

- Develop and look for resins with a much higher selectivity for NH_4^+. This would enable saline/marine waters to be treated by ion exchange. It would also better utilise capacity of the exchanger for freshwater treatment and make regeneration a lot easier due to the ease of removal of NH_4^+ under alkaline conditions.

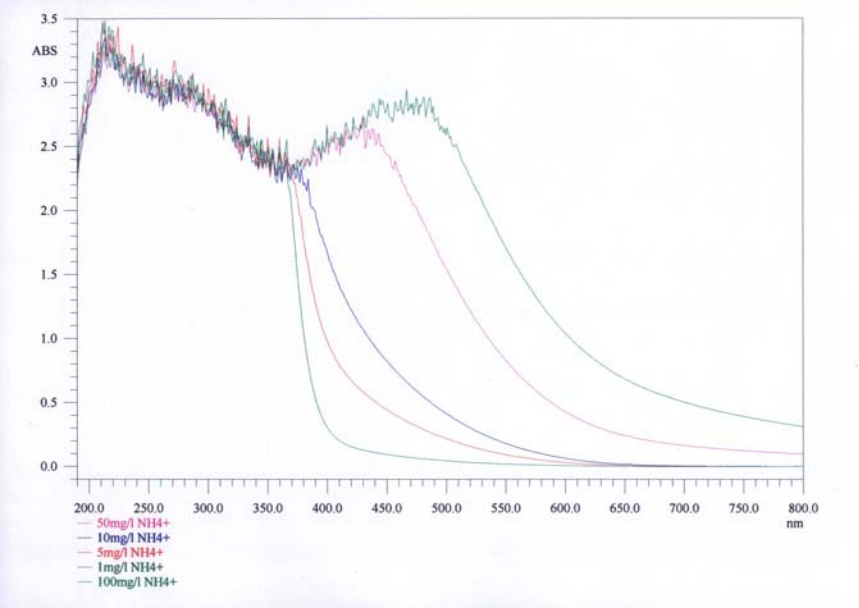
- Repeat the experiments from this project, using amines and proteins to study the effect of fouling of these compounds. Amines are usually present after the biological breakdown of proteins. It has been reported [14] that certain amines exchanged onto cationic zeolites, just like NH_4^+, however could not be removed by a number of regeneration methods. Therefore the resin became poisoned and lost all of its capacity.

- In industrial applications it is recommended that BOD should be removed prior to NH_4^+ removal by ion exchange. This is to prevent bed plugging from occurring, and the difficult task of cleaning the bed of ion exchange resin.

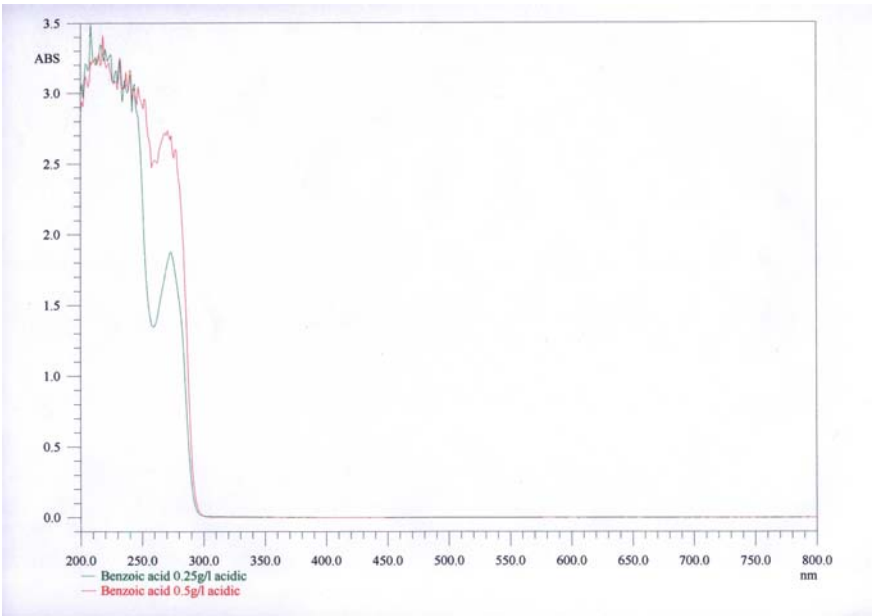
- It is recommended that future studies consider the possibility of running columns in the downflow direction to assess the potential for preventing small amounts of NH_4^+ passing through.

10.0 APPENDICES

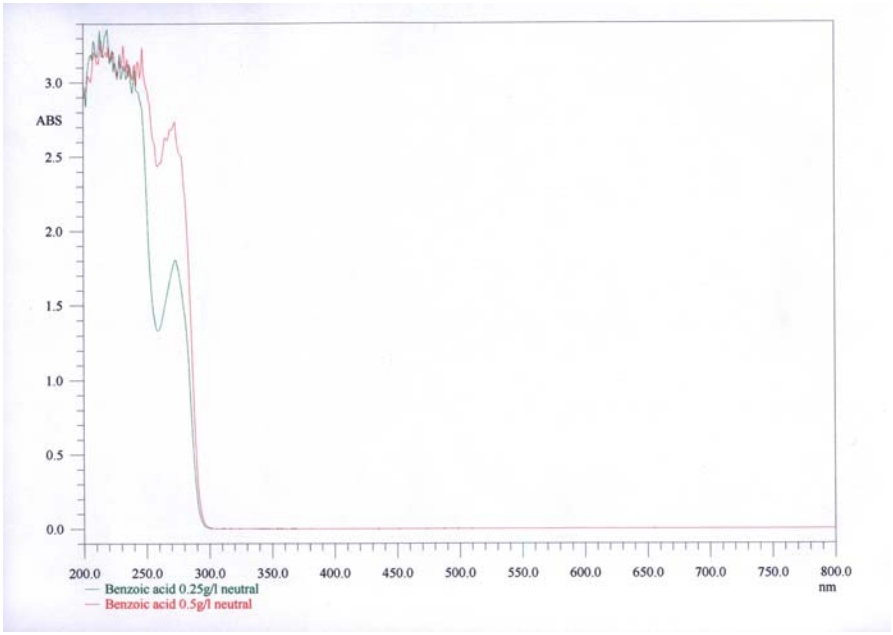
A: EXAMPLES OF UV/VIS ABSORPTION



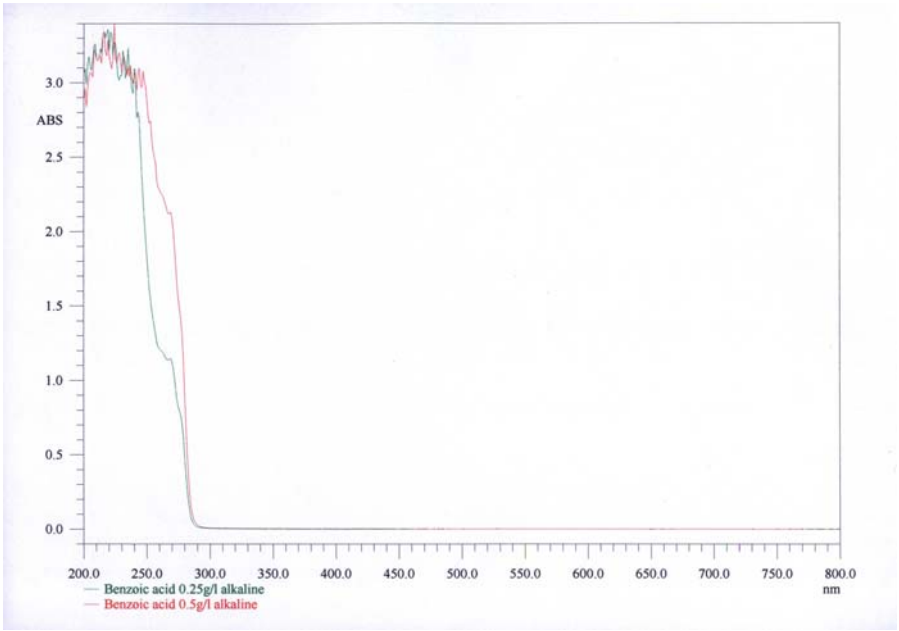
UV/vis (190nm – 800nm) absorption of ammonia and Nessler's reagent from 1mg/l – 100mg/l.



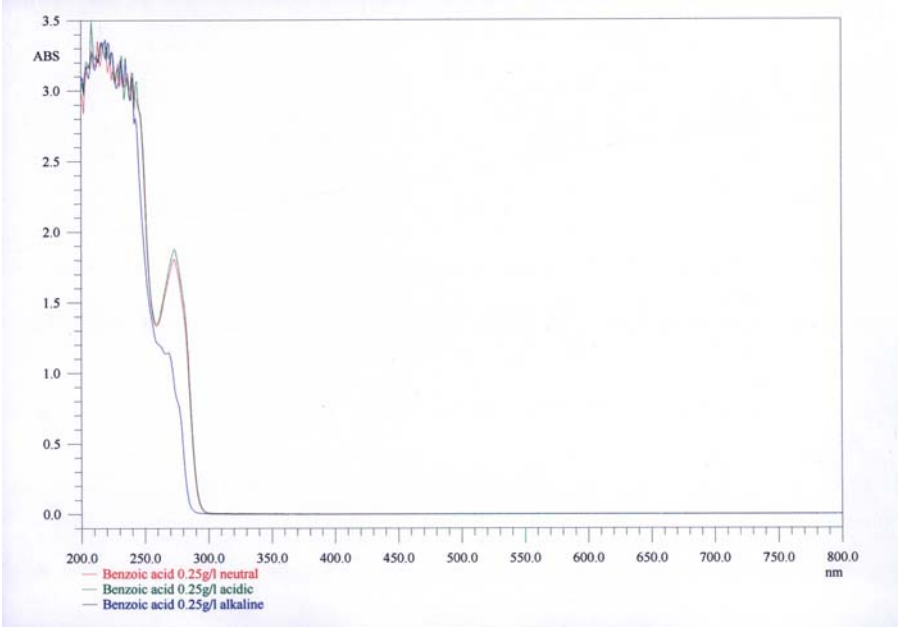
UV/vis (190nm – 800nm) absorption of benzoic acid at pH = 3.0 at two different concentrations.



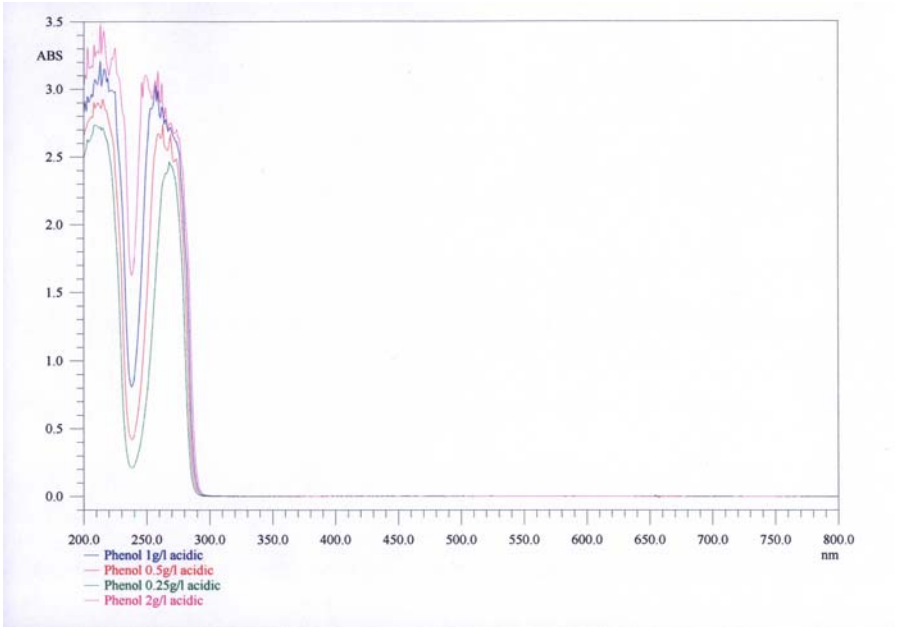
UV/vis (190nm – 800nm) absorption of benzoic acid only at two different concentrations.



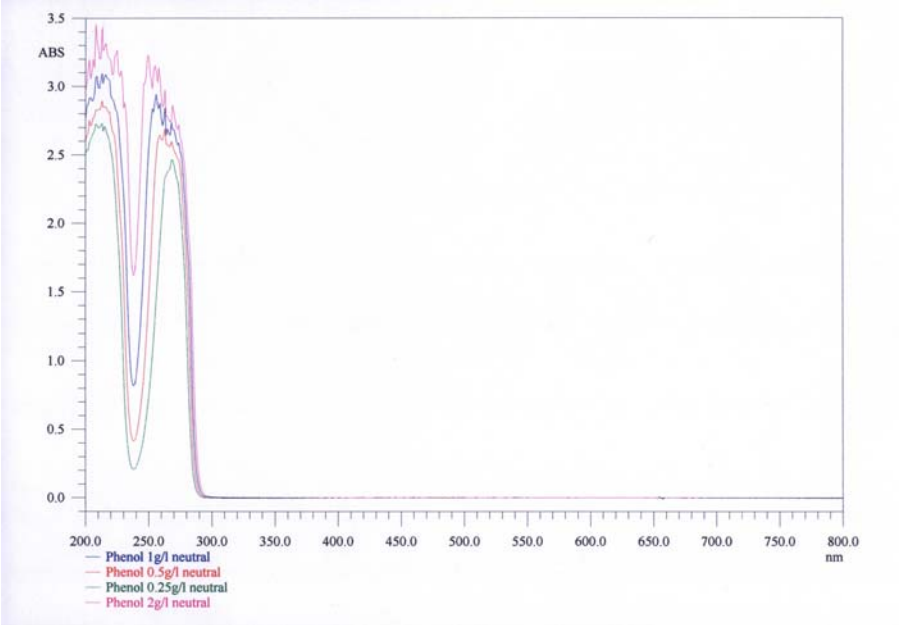
UV/vis (190nm – 800nm) absorption of benzoic acid at pH = 11.0 at two different concentrations.



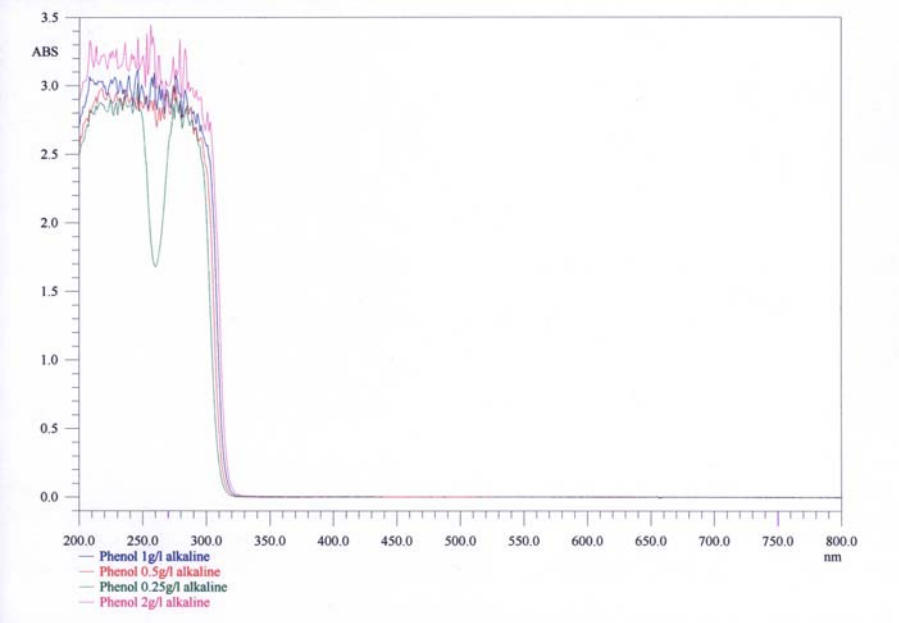
UV/vis (190nm – 800nm) absorption of benzoic acid (0.25g/l) at a range of pH from 3.0 – 11.0.



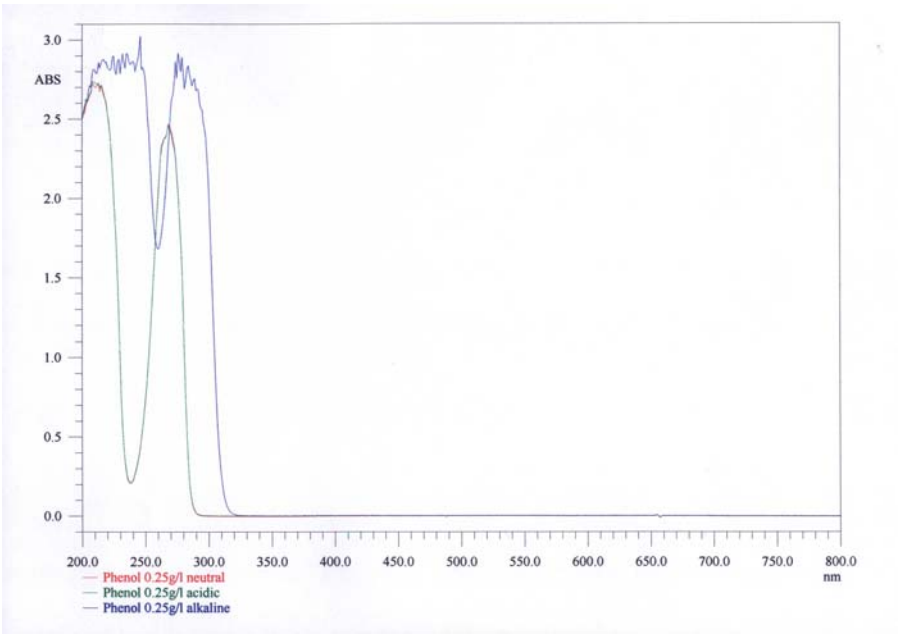
UV/vis (190nm – 800nm) absorption of phenol at pH = 3.0 at a range of concentrations.



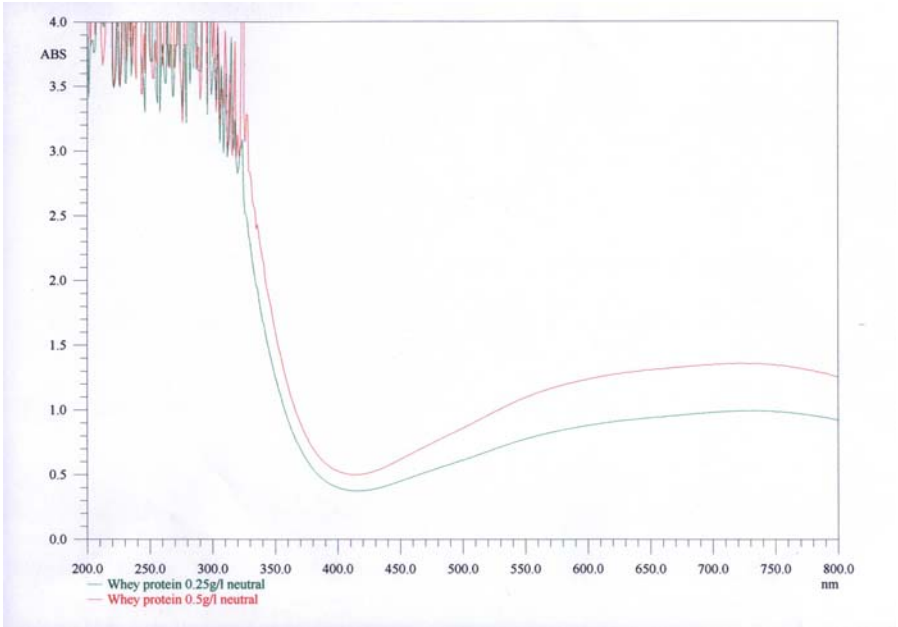
UV/vis (190nm – 800nm) absorption of phenol only at a range of concentrations.



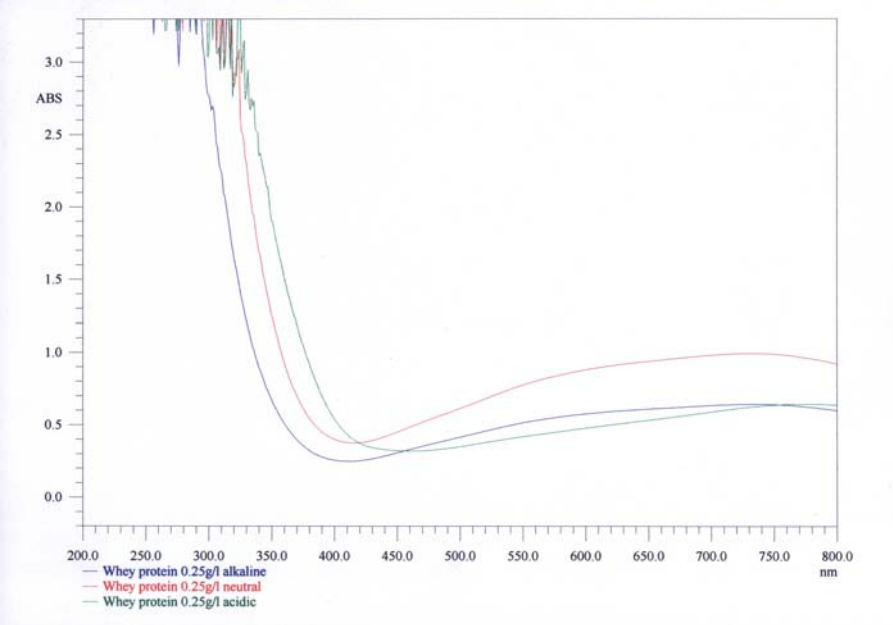
UV/vis (190nm – 800nm) absorption of phenol at pH = 11.0 at a range of concentrations.



UV/vis (190nm – 800nm) absorption of phenol (0.25g/l) at a range of pH from 3.0 – 11.0.

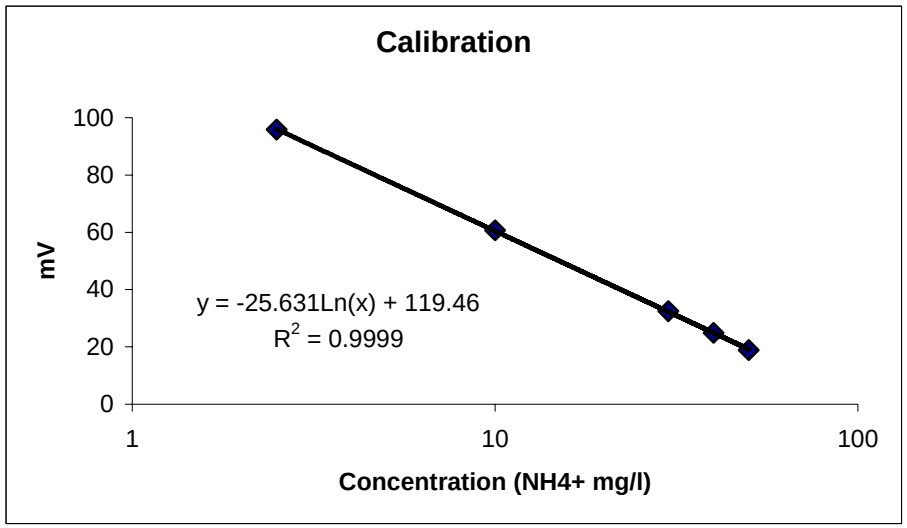


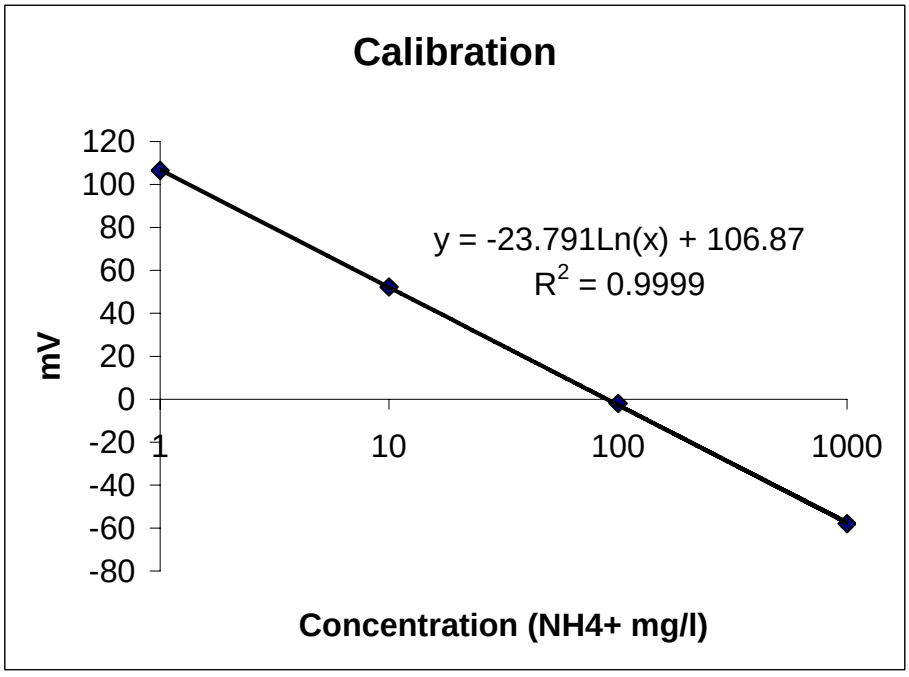
UV/vis (190nm – 800nm) absorption of protein plus the protein kit (see section 3.2.6) at two different concentrations.



UV/vis (190nm – 800nm) absorption of protein plus protein kit at a range of pH from 3.0 – 11.0.

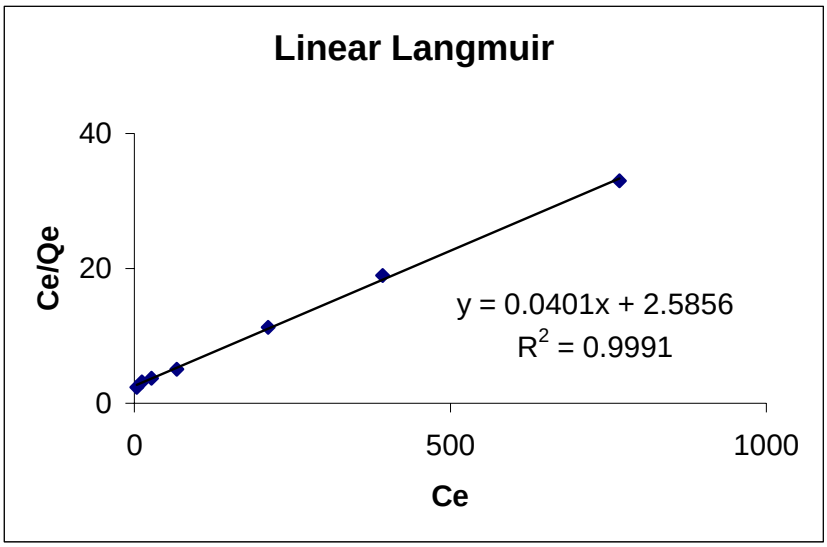
B: EXAMPLES OF PROBE CALIBRATION

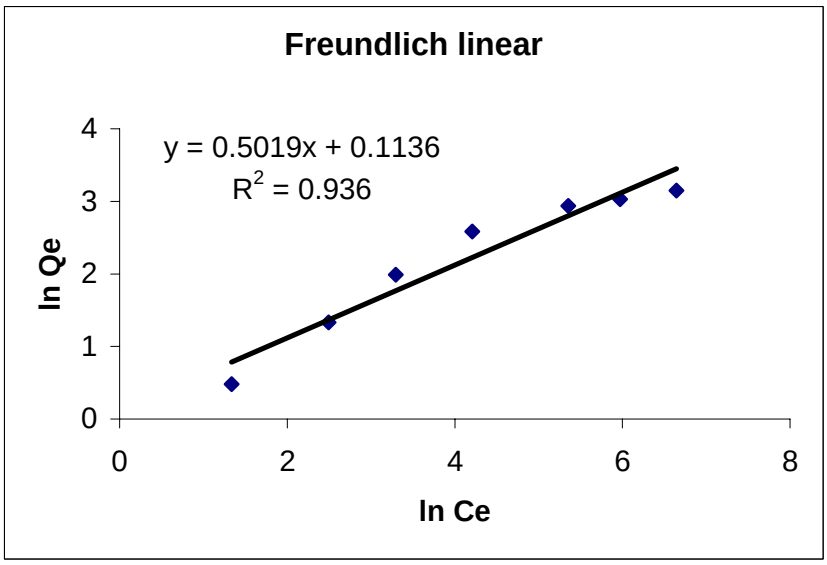




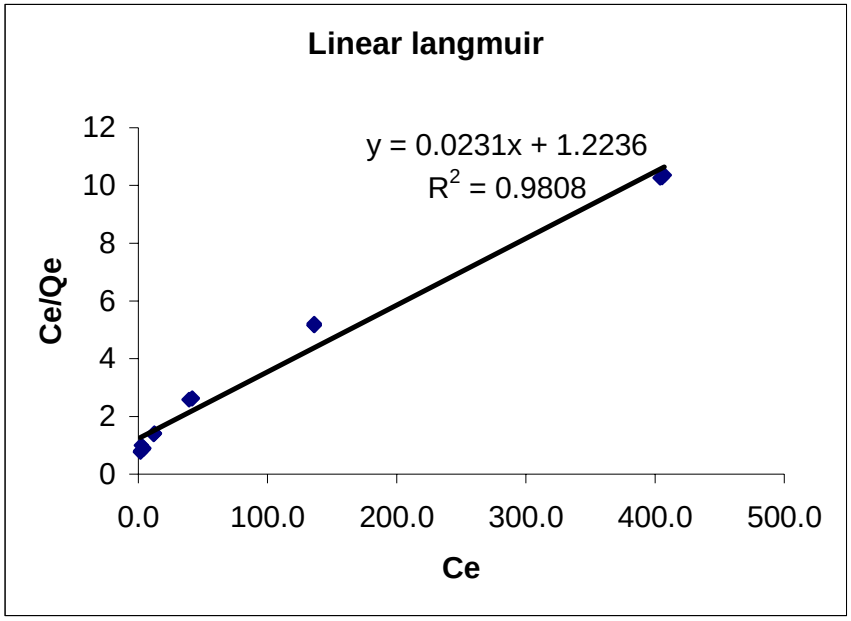
Typical calibration curves of the ammonia ion selective electrode.

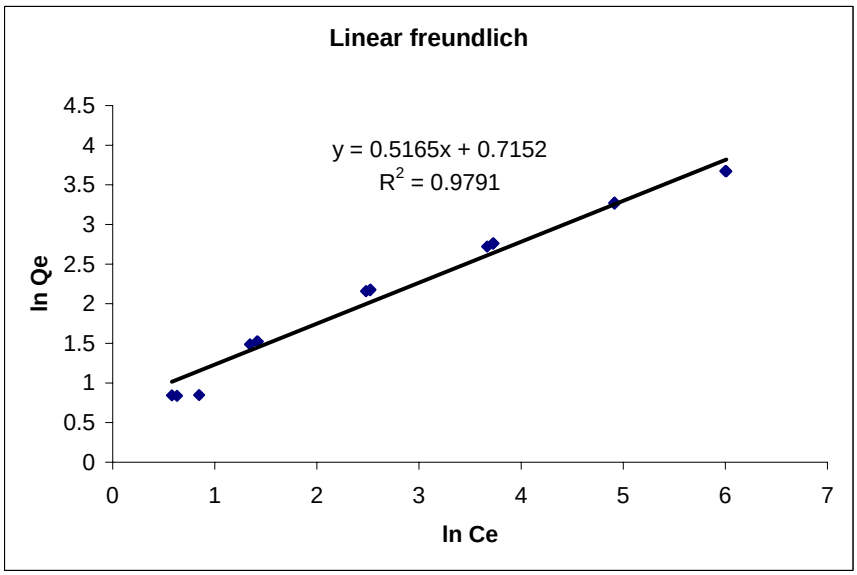
C: LINEAR FORMS OF ISOTHERM MODELS



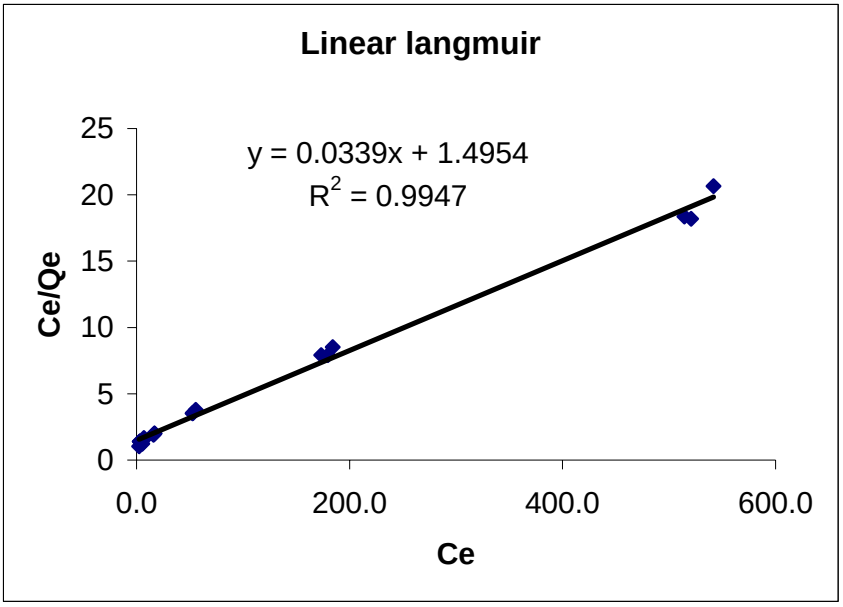


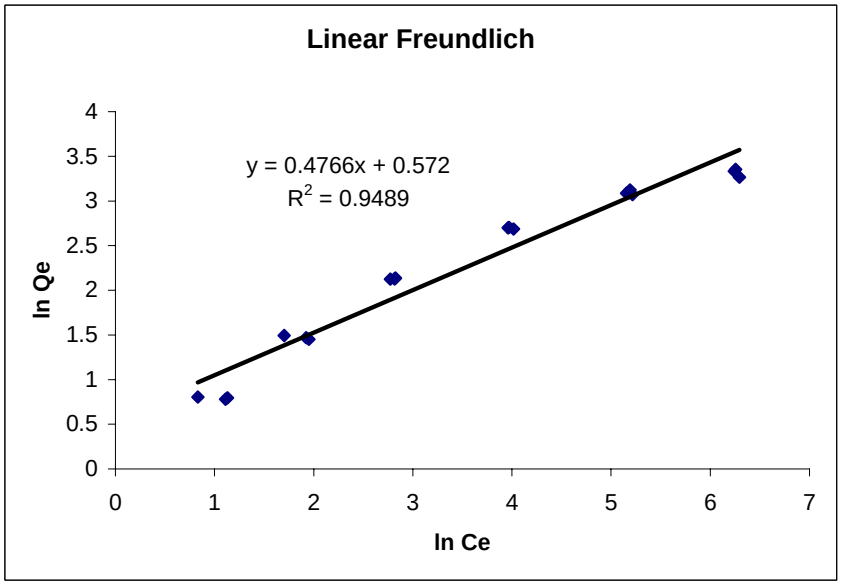
Linear forms of the Langmuir and Freundlich models onto clinoptilolite (figure 4.1).





Linear forms of the Langmuir and Freundlich models onto Dowex 50w-x8 (figure 4.14).





Linear forms of the Langmuir and Freundlich models onto Purolite MN500 (figure 4.17).

11.0 REFERENCES

Text

1. Hellferich F., (1962). ***Ion-Exchange***, McGraw-Hill Book Company Inc, San Francisco.

2. Moo-Young M., (1985). ***Comprehensive Biotechnology, Volume 1: The Principles, Applications and Regulations of Biotechnology in Industry, Agriculture and Medicine***, Pergamon Press, Toronto.

3. Nanden D., Streat M., (1984). ***Ion-Exchange Technology***, Ellis Horwood Ltd, Chichester.

4. NWSCO., (1981). ***The Report of the Water Quality Criteria Working Party***, Miscellaneous, Wellington.

5. NZWWA., (1997). ***39th Annual Conference & Expo: Conference Papers***, Ad-Vent Marketing Ltd, Birkenhead.

6. NZWWA., (1998). ***40th Annual Conference & Expo: Conference Papers***, Ad-Vent Marketing Ltd, Birkenhead.

7. Pelczar M.J., Chan E.C.S., Krieg N.R., (1993). ***Microbiology: Concepts and Applications***, McGraw-Hill inc, New York.

8. Prave P., Faust U., Sittig W., Sukatsch D.A., (1987). ***Fundamentals of Biotechnology***, VCH, Weinheim.

9. Seader J.D., Henley E.J., (1998). ***Separation Process Principles***, Wiley, New York.

10. Slater M.J., (1991). ***The Principles of Ion-Exchange Technology***, Butterworth-Heinemann Ltd, Oxford.

11. Slater M.J., (1992). ***Ion-Exchange Advances***, Elsevier Applied Science, London.

12. Tortora G.J., Funke B.R., Case C.L. (1998). ***Microbiology, An Introduction***, 6th Edn, Benjamin/Cummings, California.

13. Tschernich R.W., (1992). ***Zeolites of the World***, Geoscience Press, USA.

14. Tsitsishvili G.V., Andronikashvili T.G., Kirov G.N., Filizova L.D. (1992). ***Natural Zeolites***, 1st Edn, Ellis Horwood, London.

Thesis/Reports

15. Addison P.A., "Ion-Exchange equilibrium." *PhD research dissertation, Dep't of Chemical and Process Engineering, University of Canterbury*, 1990.

16. Dryden H.T., "Ammonium ion removal from dilute solutions and fish culture water by ion exchange." *PhD research dissertation, Dep't of Chemical & Process Engineering, Heriot-Watt University, Edinburgh*, 1984.

17. Hall R.A., "Partition of reaction products during enzymatic oil hydrolysis." *Undergraduate research report, Dep't of Chemical and Process Engineering, University of Canterbury*, 1999.

18. McVeigh R.J., "The enhancement of ammonium ion removal onto columns of clinoptilolite in the presence of nitrifying bacteria" *PhD research dissertation, Dep't of Chemical Engineering, The Queen's University of Belfast*, 1999.

19. Murray M., "Enzyme immobilisation for the lipolytic hydrolysis of vegetable oil." *Postdoctoral report, Dep't of Chemical Engineering, The Queen's University of Belfast*, 1999.

20. Walker G.M., "Industrial wastewater treatment using biological activated carbon." *PhD research dissertation, Dep't of Chemical Engineering, The Queen's University of Belfast*, 1995.

21. Woods N., "The removal of ammonia from industrial wastewater." *MSc research dissertation, Dep't of Chemical Engineering, The Queen's University of Belfast*, 1997.

Journal articles & conferences

22. Allen S J., Balasundaram V., (1995). "Benzoate adsorption onto activated carbons from Northern Ireland lignite." *IchemE Research Event / First European Conference*, 462-465.

23. Ames L.L., (1960). "The cation sieve properties of clinoptilolite." *The American Mineralogist*, **45**.

24. Ames L.L., (1961). "Cation sieve properties of the open zeolites chabazite, mordenite, erionite, and clinoptilolite." *The American Mineralogist, **46***.

25. Ballinger S.J., Head I.M., Curtis T.P., Godley A.R., (1998). "Molecular microbial ecology of nitrification in an activated sludge process treating refinery wastewater." *Water Science Technology*, **37**(4-5), 105-108.

26. Beler-Baykal B., (1998). "Clinoptilolite and multipurpose filters for upgrading effluent ammonia quality under peak loads." *Water Science Technology*, **37**(9), 235-242.

27. Beler-Baykal B., (1997), "Performance of clinoptilolite alone and in combination with sand filters for the removal of ammonia peaks from domestic wastewater." *Water Science Technology*, **35**(7), 47-54.

28. Beler-Baykal, B., Oldenburg M., Sekoulov I., (1994). "Post equalization of ammonia peaks." *Water Research*, **28**(9), 2039-2042.

29. Beler-Baykal, B., Oldenburg M., Sekoulov I., (1996). "The use of ion-exchange in ammonia removal under constant and variable loads." *Environmental Technology*, **17** 717-726.

30. Burrell P.C., Kellar J., Blackall L.L., (1998). "Microbiology of a nitrite-oxidising bioreactor." *Applied and Environmental Microbiology*, **64**(5), 1878-1883.

31. Committee on water quality criteria., (1972). "Water quality criteria". Superintendent of documents, Washington D.C.

32. Council of the European Union., (1980). "E.E.C. directive related to the quality of water for human consumption." (80/778/EEC).

33. Dale J. A., Nikitin N.V., Moore R., Opperman D., Crooks G., Naden D., Belsten E., Jenkins P., (2000). "Macronet, The birth and development of a technology." *Ion exchange at the millennium. Proceedings of IEX 2000*, 261-268.

34. Dryden H.T., Weatherley L.R., (1984). "Aquaculture water treatment by ion-exchange I. Capacity of Hector clinoptilolite at 0.01N – 0.05N." *Departmental library*.

35. Dryden H.T., Weatherley L.R., (1984). "Aquaculture water treatment by ion-exchange II. Selectivity studies with clinoptilolite at 0.01N." *Departmental library*.

36. Dryden H.T., Weatherley L.R., (1989). "Aquaculture water treatment by ion-exchange: continuous ammonium ion removal with clinoptilolite." *Aquaculture Engineering*, **8**, 109-126.

37. Dyson M., Threlfall D., (2000). "Ion exchange, membranes and combined technologies. Choices for the millennium." *Ion exchange at the millennium. Proceedings of IEX 2000*, 12-18.

38. Fang H., Chou M., Huang C., (1993). "Nitrification of ammonia-nitrogen in refinery wastewater." *Water Research*, **27**(12), 1761-1765.

39. Garrido J.M., Guerrero L., Mendez R., Lema J.M., (1998). "Nitrification of wastewaters from fish meal factories." *Water SA*, **24**(3), 245-249.

40. Green M., Mels A., Lahav O., Tarre S., (1996). "Biological ion-exchange process for ammonium removal from secondary effluent." *Water Science Technology*, **34**(1-2), 449-458.

41. Groeneweg J., Sellner B., Tappe W., (1994). "Ammonia oxidation in nitrosomonas at NH_3 concentrations near K_m: effects of pH and temperature." *Water Research*, **28**(12), 2561-2566.

42. Hanaki K., Wantawin C., Ohgaki S., (1989). "Effects of the activity of heterotrophs on nitrification in a suspended-growth reactor. 289-296.

43. Jorgensen S.E., Libor O., Barkacs K., Kuna L., (1978). "Equilibrium and capacity data of clinoptilolite. *Water Research*, (13) 159-165

44. Kithome M., Paul J.W., Lavkulich L.M., Bomke A.A., (1998). "Kinetics of ammonium adsorption and desorption by the natural zeolite clinoptilolite." *Soil Science Society of America*, **62**, 622-629.

45. Koyama K., Takeuchi Y., (1977). "Clinoptilolite: the distribution of potassium atoms and its role in thermal stability." *Zeitschrift fur Kristallographie*, **145**, 216-239.

46. McVeigh R.J., Weatherley L.R., "The effect of other cations in wastewaters on the ion-exchange removal of ammonium ion." *Departmental library.*

47. McVeigh R.J., Weatherley L.R., "Study of the ion-exchange removal of ammonium from secondary treatment wastewaters using clinoptilolite." *Departmental library.*

48. McVeigh R.J., Weatherley L.R., "The enhancement of ammonium ion removal onto columns of clinoptilolite in the presence of nitrifying bacteria." *Departmental library.*

49. Medete A., (2000). "How to handle suspended solids within ion exchange resin (IER) packed bed systems. System analysis, field experience and actual solutions." *Ion exchange at the millennium. Proceedings of IEX 2000*, 69-76.

50. Nguyen, M.L., Tanner C.C., (1998). "Ammonia removal from wastewaters using natural New Zealand zeolites." *New Zealand journal of agricultural research,* **41,** 427-446.

51. Nommik H., Vahtras K., (1982) "Retention and fixation of ammonium and ammonia in soils." *Agronomy*, **22**, 123-172.

52. Orru R., Lai N., Cincotti A., Cao G., (2000). "Utilisation of Sardinian natural clinoptilolites for heavy metals and ammonium removal." *Ion exchange at the millennium. Proceedings of IEX 2000,* 158-165.

53. Semmens M.J., Booth A.C., Tauxe G.W., (1978)., (1978). "Clinoptilolite column ammonia removal model." *Journal of the Environmental Engineering Division*, 231-244.

54. Semmens M., Klieve J., Schnobrich D., Tauxe G.W., (1980). "Modelling ammonium exchange and regeneration on clinoptilolite."

55. Singh G., Prasad B., (1997) "Removal of ammonia from coke-plant wastewater by using synthetic zeolite." *Water Environment Research*, **69**(2), 157-161.

56. Spector M., (1998) "Cocurrent biological nitrification and denitrification in wastewater treatment." *Water Environment Research*, **70**(7), 1242-1247.

57. Stanley S.O., Pearson T.H., Brown C.M., "Chapter 6. Marine microbial ecosystems and the degradation of organic pollutants." 60-79.

58. Surmacz-Gorska J., Cichon A., Miksch K., (1997) "Nitrogen removal from wastewater with high ammonia nitrogen concentration via shorter nitrification and denitrification." *Water Science Technology*, **36**(10), 73-78.

59. Walker G.M., Weatherley L.R., (1997). "Adsorption of acid dyes on to granular activated carbon in fixed beds." *Water Research*, **31**(8), 2093-2101.

60. Walker G.M., Weatherley L.R., (1998). "Bacterial regeneration in biological activated carbon systems." *Trans IchemE*, **76**(B), 177-182.

61. Walker G.M., Weatherley L.R., (1998). "Fixed bed adsorption of acid dyes onto activated carbon." *Environmental Pollution*, **99**, 133-136.

62. Wiesman U., (1994). "Biological nitrogen removal from wastewater." *Advances in Biochemical Engineering/Biotechnology*, **51**, 113-154.

63. Welander U., Henryson T., (1998). "Degradation of organic compounds in a municipal landfill leachate treated in a suspended-carrier biofilm process." *Water Environment Research*, **70**(7), 1236-1241.

64. Yang L., (1997). "Investigation of nitrification by co-immobilised nitrifying bacteria and zeolite in a batchwise fluidised bed." *Water Science Technology*, **35**(8), 169-175.